68(22)-2749/B1183-002

SUMMARY REPORT, TASK IV

Contract Number 951720

March 1, 1968
(Revised 27 May 1968)

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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.

ABSTRACT

Analytical and experimental investigations are reported concerning the Dual Mode Hydrazine System for attitude control and maneuvering propulsion of an advanced interplanetary space probe. The fundamentals of hydrazine electrolysis, including stoichiometry, electrolyte and electrode properties, materials compatibilities, power requirements, and reaction controllability are included. In addition, the problems of zero-g operation are considered. It is concluded that there are no fundamental obstacles to construction and test of a developmental model hydrazine electrolysis assembly; materials and a preliminary design are selected.

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I. Introduction and Summary

This report is a summary of work performed under Task IV of JPL Contract 951720, during the period August 1, 1967 - February 1, 1968. The objective of Task IV was to conduct experimental and analytical work in the electrolysis of hydrazine to provide gases for spacecraft attitude control. The information acquired is to be used in Task V to fabricate and test a developmental model of the Dual Mode Hydrazine System. In the latter system, devised at Hughes and analyzed in detail under Tasks I-III of the contract, the electrolysis gases are employed to provide attitude control gas pulsing and the liquid hydrazine from the same tank is fed to catalytic engines for higher thrust maneuvering functions. The potential advantages of the system have been summarized in a recent paper.* The present study was concerned with meeting the requirements of the specific mission analyzed under Tasks I-III. That mission was a large interplanetary probe-lander of the Voyager class.

The work reported here has shown that there are no fundamental problems to be overcome in reducing the Dual Mode Hydrazine System to practice. The remaining areas of uncertainty are best attacked during test of the developmental model of Task V. The results in the various areas of investigation are summarized below.

A. Controllability

Deliberate attempts to initiate uncontrolled hydrazine decomposition under electrolysis conditions have been unsuccessful. These tests have involved experiments at elevated temperatures and pressures in a bomb, and laboratory scale glassware tests in which small wires shorting the electrodes were burned out, simulating hot spots. It was concluded that a cell may be constructed which has a large tolerance to inadvertent hot spots, and that the heat released by electrolysis is largely dissipated in heat of vaporization.

A review of the literature indicated that hydrazine explosions are likely only in the event of formation of undiluted, superheated hydrazine vapor. Thermodynamic calculations showed that such an occurrence would be very unlikely in practice.

Pressurization by electrolysis, up to 600 psia, was demonstrated several times. The pressure rise was smooth, and was directly related to the amount of electrical energy used.

W. H. Jones and W. W. Butcher, "Hydrazine Electrolysis for Microthrust Applications; The Dual Hydrazine System", Hydrazine Monopropellant Technology Symposium, Naval Air Systems Command, November 28-30, 1967. CPIA Publication No. 160.

B. Electrolytes

A survey of the literature revealed no information on the electrolysis of pure hydrazine, but all evidence from aqueous solution studies indicates that only hydrogen and nitrogen gases will be produced under most conditions. Experiments at HAC gave only those gases on electrolysis of commercial hydrazine.

Several candidate electrolytes were procured or prepared, and studies carried out of solubility, conductivity, and compatibility. The most promising was dihydrazinium oxalate (equivalent to oxalic acid in solution). This material will give adequate conductivity at very low (<1%) concentrations, exhibits the necessary compatibility properties, and is not likely to have an adverse effect on the operation of the catalytic engines.

C. Electrodes

A number of metals were tried as anode materials, including stainless steels, gold, platinum and silver. In all cases, corrosive attack was evidenced at sufficiently high voltages. Although some of them, particularly silver, might prove usable under restricted conditions, the most attractive candidates for the anode were graphite and carbon. These materials showed no corrosion at potentials up to 28 volts, i.e. spacecraft bus voltage. A possible problem is mechanical attrition of the electrode after extended periods of electrolysis, but it is anticipated that selection of a suitable kind of graphite or carbon will not be difficult. For the cathode, any of a number of metals is suitable; either aluminum or a stainless steel will be used in Task V.

D. Power Requirements

An analysis was made of the probable electrolysis cell power requirements for the mission.

E. Wicking Materials

Analysis of the wicking requirements for the mission showed them to be very modest; the principal criteria for selection were accordingly structural stability and compatibility rather than rapid wicking action. A number of kinds of materials were tested. The most appropriate was found to be glass cloth .

F. Compatibility

Available information on hydrazine compatibility with the materials of interest was reviewed, and laboratory experiments conducted. It was concluded that the developmental model cell of Task V should be constructed of 6Al-4V titanium, aluminum, graphite, 99+% silica glass cloth, 304 stainless steel, Teflon, and polypropylene. No serious compatibility problems are foreseen.

G. Zero-g Design

The problems of delivering liquid-free gas to the attitude control thrusters and gas-free liquid to the catalytic engines were analyzed on the basis of available theory. It was found that the liquid expulsion requirements are probably within the capability of existing surface-tension screen devices, and further work in that area under the present contract would not be worthwhile. Several designs for the gas vent side were considered, and a configuration selected which takes advantage of the fact that in the Dual Mode Hydrazine System the gas may be generated as required in a known location. A laboratory model was constructed and tested successfully at -1g.

H. Gas Solubilities

Review of available literature indicated that the electrolysis products, gaseous nitrogen and hydrogen, are not appreciably soluble in hydrazine.

II. Literature Review

There are several aspects of the hydrazine electrolysis process which are of particular interest from the standpoint of propulsion. It is first necessary to know the composition of the gases formed: the lowest molecular weight, and therefore highest specific impulse, mixture is that resulting from formation of the elements N_2 (g) and H_2 (g); intermediate decomposition products such as ammonia would give lower performance. Secondly, the solubilities of the product gases in the hydrazine must be known, since the lesser the solubility the more efficient the pressurization process and the smaller the change in liquid composition as electrolysis proceeds. In the third place, the kind and amount, if any, of required added electrolyte must be defined, and the resulting effect on the performance of the catalytic liquid engines known.

As will be discussed later, the electrolysis of hydrazine is an exothermic process. Accordingly, it was also desirable to review the literature concerning the thermal decomposition processes of hydrazine, in order to evaluate the probable controllability of the electrolytic process.

A. Electrolysis

Although aqueous solutions of hydrazine have been studied by a number of investigators, no work has been reported concerning the electrolysis of pure hydrazine. In fact, very little has been reported on the electrolysis of either organic or inorganic solvents other than water (1).

The studies in aqueous solutions indicate that the normal hydrazine electrolysis products are gaseous nitrogen and hydrogen, at anode and cathode respectively. Other products, such as ammonia, hydrazoic acid and more complex nitrogen compounds, may be formed at high current density, particularly in the presence of certain ions. Sulfate, for example, can be oxidized to persulfate if current density and cell voltage are high enough. In that case, the oxidation to abnormal products is apparently by persulfate rather than at an electrode. One item of special interest was reported by Turrentine and Gibbons (2), who electrolyzed hydrazine carbonate in cold solution at high current density. These conditions presumably would be favorable to the formation of percarbonate and abnormal oxidation products of hydrazine. Nevertheless, nitrogen was the only product at the anode. This result is favorable because trace amounts of atmospheric carbon dioxide are likely hydrazine contaminants.

Evidence concerning the mechanisms of the electrode reactions in hydrazine electrolysis is meager and conflicting (4-6). These results will not be reviewed here, because they are all derived from aqueous systems and their applicability to neat hydrazine is questionable. In reducing the dual mode hydrazine system to practice, conditions will be selected which give the normal electrolysis products; the mechanism of their formation is of no practical concern.

B. Solubilities

The gaseous products of hydrazine electrolysis will to some extent dissolve in the liquid hydrazine. This fact will lead to some inefficiency in pressurization, and some loss of gas through firing of the liquid engines. If only the gas-side thrusters were used, there would, of course, be no total gas loss over the entire mission. As will be shown, the available information indicates that virtually all of the ammonia and none of the hydrogen and nitrogen resulting from hydrazine decomposition will dissolve in the remaining liquid.

To take a specific case, we may consider the 3600 lb-sec. total impulse requirement for the mission. If half of this is employed for the liquid engines at an I_{sp} of 230 seconds and the other half for cold gas attitude control at an I_{sp} of 120 seconds, the total tank volume will be of the order of 11,000 cm^3 and the volume of propellant for the liquid engines about 3500 cm^3. Consider a tank pressure of 200 psia (13.6 atm.) and a temperature of 25°C (77°F). We may then estimate from solubility data what fraction of the total gases generated could be lost through the liquid thrusters. If the pressurization occurs by the reaction N_2H_4 (ℓ) = N_2 (g) + $2H_2$(g), then to a first approximation, $P_{N_2}^{g}$ = 4.5 atm., and $P_{H_2}^{g}$ = 9.1 atm.

1. Nitrogen

Three references (7-9) were found concerning the solubility of gaseous nitrogen in hydrazine. Representative data, reduced to a common basis, are given in Table I. The results were obtained by different techniques, with different hydrazine purities, and are probably of differing validities.

Because the solubility of a gas in a liquid is approximately proportional to the partial pressure of the gas, the data of Table 1 can be converted to a common basis, Table II compares the three sources of data at 200 psia. (Note that no correction is made for the effect of vapor pressure of hydrazine, which is small). It will be seen that there is a large difference between the Aerojet and the other data. The Aerojet data are more recent and were obtained at pressures closer to those of practical interest.

The above results may be applied to the specific case given previously, i.e. for 3500 ml hydrazine, 7500 ml ullage at 200 psia and 77°F. If the gas composition is approximately (N_2 + $2H_2$), the data of Table 2 indicate that 0.1% of the nitrogen generated dissolves in the hydrazine, based on the Aerojet results; or 5%, based in the NOTS results. It is probable that the Aerojet data are more applicable to the present situation, but even if the higher figure were correct, it seems unlikely that the operation of the catalytic engines would be seriously affected.

2. Hydrogen

Hydrogen solubility data for hydrazine were found only in reference 7 (NOTS). It is reported that the solubility is "very low", about 1.6×10^{-5} wt%

TABLE I

NITROGEN GAS SOLUBILITY IN HYDRAZINE

Reference	P, psia*	T, °F	Solubility, Wt. %
NOTS (7)	14.7	86	0.0125
	1.41	86	0.0013
Bell (8)	76.4	72.2	0.0
	76.7	46.4	0.04 ± 0.03
Aerojet (9)	300	86	0.0059
	300	72	0.0052
	300	46	0.0047
	700	86	0.0115
	700	72	0.0098
	700	46	0.0086

*For Reference 7, P is the partial pressure of nitrogen; the others refer to total gas pressure, including the hydrazine vapor pressure. For the accuracy of the present treatment, the correction is unimportant.

TABLE II

NITROGEN GAS SOLUBILITY IN HYDRAZINE
AT 200 PSIA GAS PRESSURE

REFERENCE	T, °F	SOLUBILITY, WT. %
NOTS (7)	86	0.17
Bell (8)	46.4	0.10 ± 0.08
Aerojet (9)	77	0.0035
	46	0.0031
	86	0.0039

at 650 mm pressure and 30°C. For the above specific case, this figure leads to an estimate that 0.1% of the generated hydrogen dissolves in the hydrazine.

3. Ammonia

There remains the question of abnormal electrolysis products, particularly ammonia. In reference (10) a solubility of 4.472 g NH_3/100g N_2H_4 at 1 atmosphere is reported. Simple calculations from this value show that virtually all of any ammonia formed on electrolysis will dissolve in the hydrazine.

C. Decomposition Reactions of Hydrazine

At ordinary temperature, the hydrazine molecule is metastable with respect to a variety of decomposition products. Once the necessary activation energy has been acquired, the decomposition reaction gives hydrogen, nitrogen, and a variable amount of ammonia as the ultimate products. The mechanism by which the reaction occurs may be complex, because of the many possible intermediate species. A number of radicals, ions, and molecular species possibly could be part of the reaction.

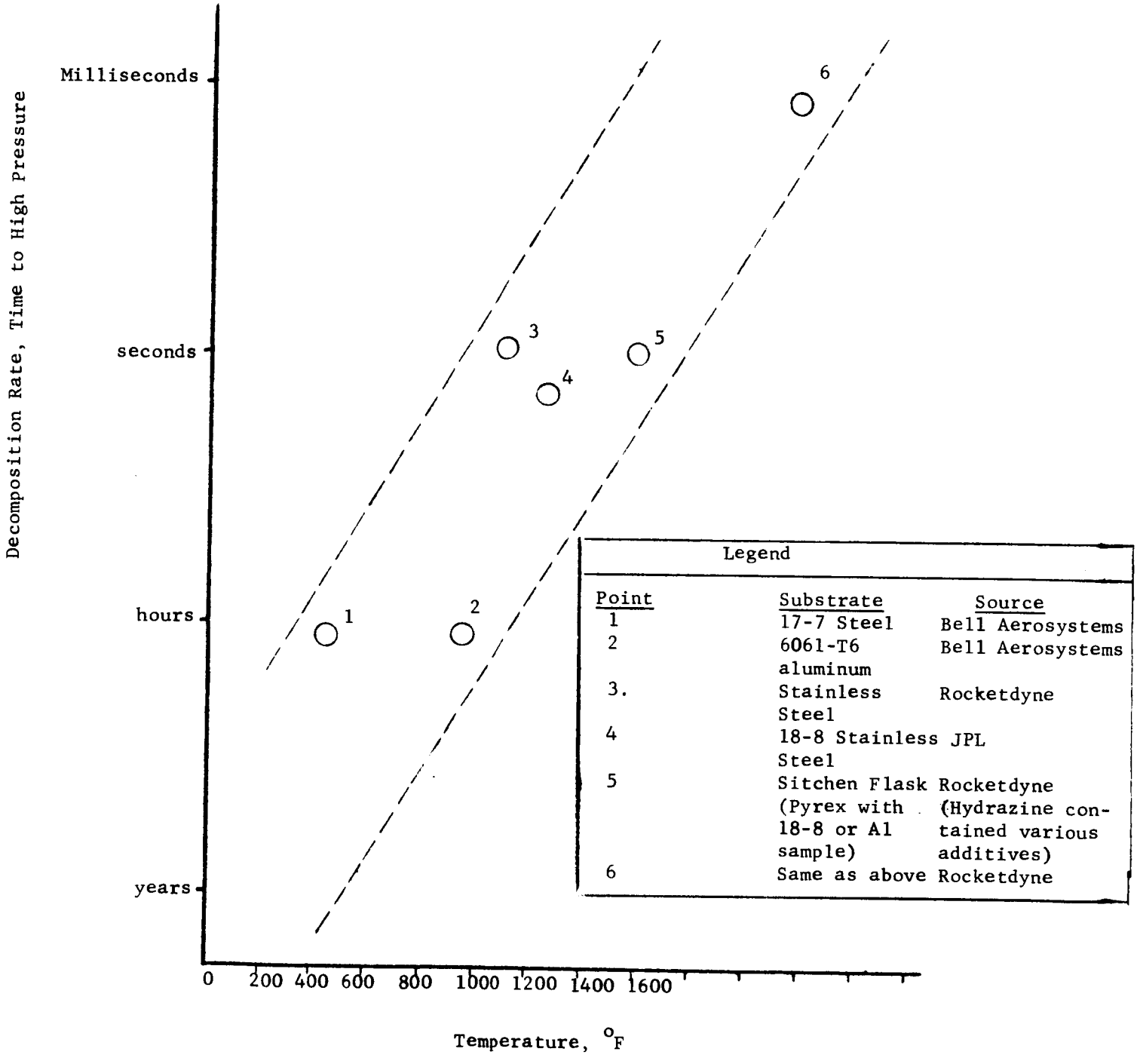
The reactions may be classified into two general groups: homogeneous and heterogeneous. As in the study of most other chemical reactions, the homogeneous types are much easier to investigate, and most of the information is of these types. The evidence to date indicates that the decomposition reaction is principally a gas-phase process, with explosions arising from heterogeneous decomposition of gaseous hydrazine. In the absence of a catalytic surface or oxygen, the liquid has been heated to above 500°F without decomposition.

A number of high temperature studies (>1000°K), including flame, shock tube, and flow reactor experiments, are available; these investigations have been largely concerned with acquisition of kinetic and mechanistic information concerning the homogeneous gas-phase reaction. Relatively few low-temperature studies are to be found. Some recent reviews are given in References 11-13; experimental information is found in Reference 14-16. A number of different mechanisms have been proposed, but regardless of which is correct, the first step of the homogeneous reaction is relatively certain: dissociation of hydrazine to amino radicals. The succeeding steps are radical reactions in all cases. It should be noted that this conclusion refers to normal thermal decomposition rather than detonation. The mechanism of the latter is probably different, as will be mentioned later.

A main point of the literature results is that at ordinary temperatures the homogeneous rate is generally small compared with the heterogeneous rate. The data shown in Figure 1 are typical of those reported for decomposition on common metals. Generally speaking, the trend is towards less importance of the substrate composition at higher temperatures, with most weakly catalytic surfaces becoming equivalent at about 1000°F.

FIGURE 5

TREND OF THERMAL DECOMPOSITION RATES OF LIQUID HYDRAZINE AS A FUNCTION OF TEMPERATURE ON RELATIVELY NON-CATALYTIC SURFACES



The surface-induced decomposition may involve liquid as well as gaseous hydrazine; the evidence is not entirely clear. In early experiments, Lucien (17) reported that hydrazine introduced into mercury-filled glass tubes without initial ullage space behaved as though the reaction occurred at the liquid-glass interface. Later analyses, however, indicated the results could be interpreted equally well on the basis of a process controlled by vaporization rate. Likewise, the isothermal bomb experiments of Thomas (Reference 18) may be vaporization-controlled.

Interpretation of reported hydrazine compatibility data is sometimes clouded by the fact that measurements are made in glass apparatus. Heterogeneous catalysis almost inevitably requires adsorption of the reactant molecule on the catalyst surface. This process is expected to be somewhat different for hydrazine adsorption on glass compared with adsorption on metals.

Metals may be divided into two groups: the relatively noncatalytic group typified by Au, Cd, Mg and Al, and the highly catalytic group which includes Cr, Mn, Fe, Ni, Pt Ir and Cu. Inspection of the electronic structure of these elements suggests that incomplete d-orbitals may be a key feature of the catalytic group. When orbital sharing is possible, such as by free electrons of the hydrazine molecule, the overall energy of a system is reduced, as commonly manifested by release of heat of surface adsorption. Orbital sharing also tends to reduce, or at least alter, the energy level of the possible excited states and, in consequence, the activation energy required for the rearrangement of molecular bonds. That adsorption bonding by the unshared eldctrons on the nitrogen atom is important is verified by the observation that ammonia is a poison for Shell 405 catalyst. The ammonia presumably is adsorbed on reactive sites in the same manner as hydrazine, thereby reducing the available surface area. Vacuum removes absorbed ammonia and returns the catalyst to full strength. Few details are known of the mechanism of decomposition of a hydrazine molecule adsorbed on metallic surfaces. It has been suggested (13) that a dissociation to amino radicals may be the first step, analogous to the homogeneous reaction, but there would not appear to be any direct evidence of radical formation.

In the case of glass or silica surfaces, the experimental evidence is reasonably conclusive: dissociation to radicals does not occur. Szwarc (19) noted that decomposition in the presence of toluene produced dibenzyl in proportion to the amount of amino radicals, and increasing the surface area of the reactor increased overall reaction rate, but did not affect dibenzyl production, indicating the amino radicals were produced only by the homogeneous reaction. In addition, Kant and McMahon (20) studied decomposition of nitrogen-15 labeled hydrazine in glass vessels and found that the nitrogen gas was produced without rupture of the original N-N bond; this fact precludes formation of amino radicals. Further evidence for absence of radicals was reported by Birse and Melville (21), who decomposed hydrazine on glass in the presence of para-hydrogen. No o-p conversion was observed, as would have happened in the presence of a very low free radical concentration. It is not surprising that the mechanism of decomposition is different on glass and a metal because the absorption process is not the same.

The glass has no atoms with unfilled d-orbitals available for bonding, but the combined oxygen atoms are sufficiently electronegative to attract electropositive hydrogen atoms strongly. It is likely that the hydronitrogen decomposition intermediates are also intimately associated with the glass oxygen atoms, from which may derive the friving force for the reaction.

Adsorption in a configuration favorable for decomposition might be expected to be easier on metal than on glass because of the steric factors involved. The metal is a regular array of atoms in a crystal network and bonding should take place through two, or perhaps only one, nitrogen atoms. With glass, however, four or more elastrostatic bonds between the hydrogen atoms of the hydrazine and the oxygen atoms of the glass may be needed. Glass, being normally non-crystalline, may have few or many sites which are catalytically active, depending on the frequency of occurrence of atoms in the proper configuration. Much of the adsorbed hydrazine may be on non-reactive sites or improperly adsorbed on active sites.

If it is proper to assume that adsorption in a reactive configuration is easier or metal than on glass, it is still not proper to assume the reaction rate will be faster because that also depends on the activation energy. There is not sufficient information to estimate that energy, and hence overall reaction rate. It would, however, appear that inherent randomness in configuration of the glass atoms and more positions in which hydrazine could be adsorbed would lead to more variability in overall reaction rate for glass than for metals.

The major area of concern in inducing hydrazine decomposition is the possibility of detonation. Detonations and thermal explosions have been encountered throughout the development of hydrazine as a propellant, and one of the obstacles to its early use was adequate demonstration of detonation-free behavior under operational circumstances. The explosions were generally attributed to reaction of the vapor, and suitable control of the vapor phase decomposition was a major objective of much of the effort.

It is indeed likely that hydrazine explosions are initiated in the gaseous phase. Liquid hydrazine is very insensitive to impact and friction. Standard tetryl booster charge failed to induce detonation. Initiation may be achieved, by a vigorous initiator, and ballistic mortar tests showed that hydrazine possessed 135 percent of the strength of TNT. Spark sensitivity is reported to be several joules, depending on the degree of confinement, with only partial decomposition of the hydrazine.

Hydrazine vapor is considerably more hazardous than the liquid. Pure vapor or mixture with other gases will propagate spark-initiated detonation if the composition is within the inflammability limits. According to the Bureau of Mines (22), explosion may take place at 84^{o}F (vapor pressure of 12 mm) with pure vapor, but no observable decomposition of remaining liquid hydrazine occurs of liquid contribution is uncertain.

From the evidence, it seems reasonable to ascribe the higher hazard of hydrazine vapor principally to its ability to propagate detonation. Further, the relative rates of the normal homogeneous and heterogeneous reactions strongly suggest that catalytic initiation at some point on the walls of the system would present the greatest hazard. Catalytic initiation at the liquid-wall interface would be possible, but unlikely to result in a reaction other than normal decomposition.

The ability of the liquid to damp an explosive reaction might be the result of the large heat of vaporization of hydrazine. It is a requirement for explosion that heat be produced faster than it is dissipated to the surroundings. The heat liberated in explosion of liquid hydrazine is probably on the order of 23 kcal/mol, only about twice the heat of vaporization. A liquid, having many molecules in close proximity, could dissipate combustion heat more effectively by transfer to adjacent molecules as heat of vaporization and increase in liquid enthalpy. That heat transfer is a critical parameter is further demonstrated by the fact that dilution of hydrazine vapor by an inert gas reduces inflammability and explosion hazard. No direct experimental investigation of random hydrazine detonations is known.

III Electrolytes

A. General Requirements

The electrical conductivity of pure hydrazine is very low ($\sim 2.5 \times 10^{-6}$ mho cm^{-1} @ 25°C; Reference 23), and it is probable that a certain amount of an electrolyte must be present to provide a liquid sufficiently conductive to provide reasonable rate of electrolysis. Commercial hydrazine is not pure hydrazine, it should be noted, and accordingly some conductivity is generally available in the usual propellant. Definition of the required conductivity must follow from specific mission requirements, as will be discussed later.

There are several general requirements for selection of an electrolyte:

1. There should be no abnormal electrolysis products under operating conditions, i.e. a gaseous mixture of composition $N_2/2H_2$ should be obtained exclusively.

2. The electrolyte, or any of its decomposition products under operational conditions, should not adversely affect the operation of the catalytic hydrazine thrusters.

3. The conductivity of the electrolyte solution must be high enough that only very small amounts (less than 1%) need by added, to avoid considerable effects on propellant chemical, physical, or ballistic properties.

4. The solubility of the electrolyte must be sufficient that it remain in solution throughout the mission.

B. Conductivity Requirements

The desired conductivity of the hydrazine solution is attainable by variation of three parameters, as can be shown as follows. Consider a pair of electrodes, each of area A, separated by a distance L and at a potential difference of E. Then, by Ohm's Law,

$$E = IR = I \left(\frac{1}{K}\right) \frac{L}{A}$$

E = potential difference, volts

R = resistance, ohms

K = specific conductance (1/specific resistance)

I = current, (coul/sec) (amps)

Or, $$I = EK \frac{A}{L}$$

The number of mols of gas generated per second is directly related to the current passed. In the case of hydrazine electrolysis,

$$N_2H_4(\ell) + 4 \text{ Faradays} = N_2(g) + 2H_2(g),$$

so that

$$\text{Mols gas/sec} = \frac{3I}{4(96{,}500)} = \frac{3\,E\,K\,(\frac{A}{L})}{4(96{,}500)}$$

Hence, for a given cell geometry, the gas generation rate may be adjusted by changing the applied voltage, the specific conductance of the solution, or the electrode area. The electrode area is obviously difficult to define, particularly when a wick is employed, and in practice the effective value of the term $(\frac{A}{L})$ would be determined empirically by current measurements with solutions of known K. Values of K have been established for a number of reference salt solutions.

C. Electrolyte Investigations

A number of possible electrolytes were considered, and experimental studies conducted on several of them. Table III lists the possibilities, along with some general remarks on their suitabilities. The most promising was the oxalate. It was thought desirable to avoid underoxidized carbonaceous compounds, such as tetramethylammonium hydroxide, because of the possibility of coking in the catalyst bed of the liquid engine.

TABLE III

Electrolytes for Hydrazine Electrolysis

Electrolyte	Remarks
Oxalate	Should give volatile carbonaceous products
Formate	Less oxidized than oxalate
Nitrate	Has been used in catalytic engines; may give corrosion.
Carbonate	Likely propellant contaminant; complex reaction with hydrazine.
Sulfate	May be a catalyst poison
Tetramethylammonium Hydroxide	Volatile (no solid residue); might give carbon deposition; storage stability questionable.

The hydrazine employed in the experiments was analyzed both by the procedure described in MIL-P-26536B (Reference 29) and by another variation of the direct iodate oxidation method which has been described by the Walter Kidde Company (30). Equivalent results were obtained from the two procedures; the Walter Kidde Company method gave 99.2 $\pm$ 0.4% hydrazine while the MIL-P-26536B method gave 99.2 $\pm$ 0.2% hydrazine. Four samples were analyzed by each method.

These results indicate that the hydrazine employed contained considerably less water than the 2.5% allowed by MIL-P-26536B, and is in the neighborhood of the 0.5% water typically found in unopened drums. (31)

Analyses were also conducted for ionic contaminants. Information on the identity of possible ionic impurities in hydrazine produced by the Olin Matheson Chemical Corporation indicated that Na+ and Cl- were the major inorganic contaminants. It was also deemed likely that CO_2 absorbed from the air might form carbonates in solution and thus contribute to the conductivity of the hydrazine. Qualitative tests were therefore carried out to determine whether significant quantities of these constituents were present in the hydrazine employed in the electrolysis experiments.

a. Test for Chloride: One ml 5% $AgNO_3$ was added to a nitric acid solution containing 2 ml. hydrazine; no detectable cloudiness resulted. It is therefore concluded that no more than 10 parts per million chloride could be present in the hydrazine.

b. Test for Carbonate: Two ml. of hydrazine and 50 ml. of a solution of 10% $Ba(OH)_2$ in water were mixed. No discernible cloudiness of the solution resulted. Only 10^{-7}g CO_2 would be soluble in the solution. It was therefore concluded that no more than 30 parts per million of carbonate was present in the hydrazine.

Preparative procedures: Dihydrazinium oxalate, $(N_2H_5)_2\ C_2O_4$, was prepared by addition of excess hydrazine to a solution of oxalic acid in methanol. The resulting precipitate was washed with absolute methanol, dissolved in warm water, reprecipitated with absolute methanol, and vacuum-dried.

Hydrazinium diformate, $(N_2H_6^{++})(HCO_2^-)_2$, was prepared by dissolving reagent grade formic acid in water, adding the stoichiometric quantity of hydrazine, and recrystallizing the product from anhydrous isopropanol.

Hydrazinium nitrate, $N_2H_5^+\ NO_3^-$, was obtained by dissolving reagent-grade NH_4NO_3 in hydrazine, warming to release the ammonia, and recrystallizing the product from absolute methanol.

The melting points of the above sales were in accordance with literature values.

The tetramethylammouium hydroxide was the EKC Technical Grade, 10% aqueous solution.

Specific conductances of four electrolytes in hydrazine were determined. The results are presented in Table IV and Figure 2. At the time of measurement it had been thought that low voltages would be required to prevent electrode corrosion, so the range of conductance is somewhat higher than is now of greatest interest. The data do indicate, however, that all of these materials provide good conductivity and are potentially useful. Note that concentration is expressed as the total amount of material that would have to be added to hydrazine rather than as the hydrazinium salt. This expression is thought more meaningful in terms of performance and significance to the catalytic engines.

The stoichiometry of the electrolysis process in oxalate solutions was estimated by Orsat analysis of gas samples from high pressure bomb experiments (See Section VII-B) 48 and 49, both of which used 0.5% oxalic acid electrolyte and graphite anodes. Experiment 48 used a 304 stainless steel cathode and experiment 49 used an aluminum cathode. The results were:

	Experiment 48	Experiment 49
H_2, %(V)	60.7	64.5
N_2, %(V)	39.3	35.5

These results are suspect because neither experiment gave the expected 66.7% H_2 and 33.3% N_2. The pressure bomb used in these experiments has had a history of chronic leakage which is due to a bad seal design. Hydrogen has a much higher leakage rate than nitrogen so that leakage would result in a low hydrogen assay.

Two years ago, in a Hughes IR & D program, samples of gas from electrolysis of commercial hydrazine, with and without added hydrazine nitrate electrolyte, were analyzed by an independent laboratory (Truesdail) and found to contain between 66.0 and 66.4% hydrogen. In view of this fact and also that another, better opportunity to sample gas will arise during the Task V tests, it was decided not to rework the laboratory hardware for further analyses during Task V.

As a result of the electrolyte investigations, oxalate was selected for use in the developmental model cell of Task V.

TABLE IV

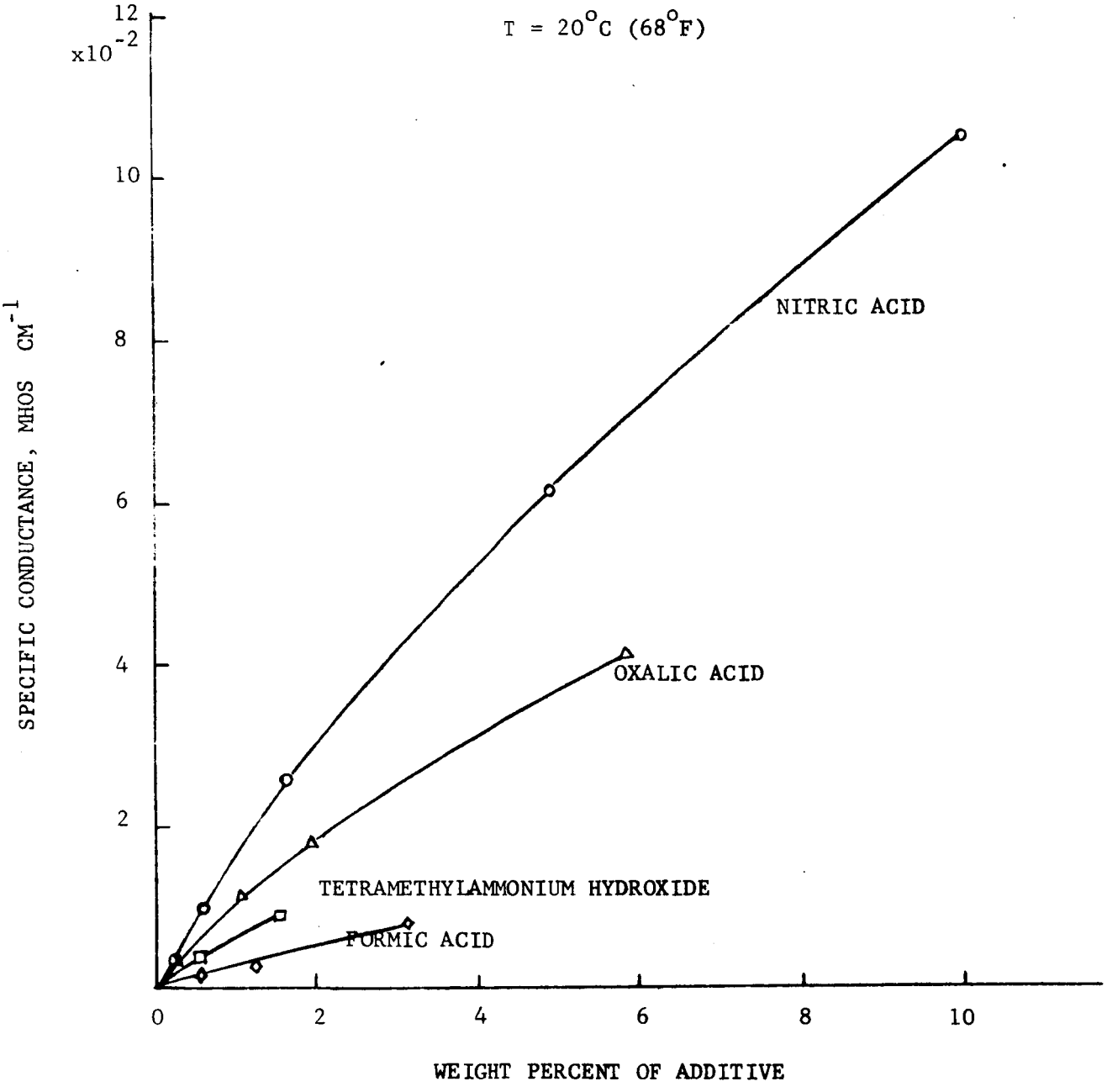
ELECTROLYTE CONDUCTIVITIES IN HYDRAZINE

ADDITIVE	WEIGHT % OF ADDITIVE	SPECIFIC CONDUCTIVITY, MHOS CM^{-1}
Oxalic Acid	0.196%	$30. \times 10^{-4}$
	0.827	51.
	1.046	110.
	1.965	180.
	5.804	410.
Formic Acid	0.473	15.
	1.245	23.
	3.13	38.
Nitric Acid	0.565	98.
	1.65	250.
	4.97	620.
	9.94	1060.
Tetramethyl-ammonium Hydroxide	0.527	29.
	1.58	73.

FIGURE 2

SPECIFIC CONDUCTANCE OF SOLUTIONS
OF VARIOUS ADDITIVES IN HYDRAZINE
AS A FUNCTION OF CONCENTRATION

T = 20°C (68°F)



IV Electrode Materials

The principal criterion for electrode selection is that the material employed not corrode under the conditions of electrolysis. In addition, structural stability is needed. Metals are good structural materials, but all metals will dissolve at the anode at sufficiently high impressed voltage. The problem is to select a voltage and electrolyte concentration which will produce sufficiently rapid electrolysis at a potential below the threshold for electrode attack. Although a minor amount of corrosion might have no appreciable effect on the electrolysis process, the possible concomitant generation of particulate matter or trace amounts of metallic ions could conceivably affect the catalytic engines in the dual mode hydrazine system.

A number of metals were tried, but none was entirely satisfactory. Stainless steels, gold, platinum, and silver all showed appreciable corrosion, although silver was found usable under restricted conditions.

The most attractive anode candidates were graphites and carbons. These materials gave no measurable corrosion at potentials up to 28 volts. i.e. up to the ordinary spacecraft bus voltage. The problem to be resolved with these materials is structural stability. It is anticipated that molded materials will be preferrable to extruded, for structural reasons. Graphites are easier to machine and less brittle than carbon. Since metallic corrosion occurred only at the anode, there is no reason to use a carbon or graphite cathode, and the cathodic material of choice will be a metal such as stainless steel or aluminum.

Electrode materials studies took the form of current-voltage measurements, electrode weight change determinations, and visual observations of the electrodes. A series of laboratory glassware experiments were followed by investigations in the high pressure bomb (described below under Controllability), Section VII. Details of the experiments follow.

Series A

Cell: (2 cm x 5 cm) stainless steel electrodes

Wick: Glass Cloth

Electrolytes:
(1) 0.5% dihydrazinium oxalate
0.8% H_2O (already present)
(2) 0.5% hydrazinium nitrate
0.8% H_2O (already present)
(3) 0.3% tetramethylammonium hydroxide
3.4% H_2O (TMAH added as aqueous solution)

Potential: 4 volts.

Results: The indicated electrolyte comparisons were selected, on the basis of some preliminary runs, to give about 100 ma current. The results were not as anticipated, however, in that erratic changes in current were observed for the oxalate and nitrate solutions over a period of more than fifty hours of electrolysis, and the solutions gave currents differing considerably, in the order oxalate > hydroxide > nitrate. The currents were in the 10-200 ma range. Late in the experiments, some black, non-adherent deposit was observed on the cathode. The amount of deposit was roughly proportional to the current.

Series B

Cell: As in A

Wick: Glass Paper

Electrolyte: Dihydrazinium oxalate, 5% and 10%

Hydrazinium formate, 5% and 10%

Potential: 2-3 volts

Results: This series was run concurrently with Series A. The currents, in line with the concentrations, were in the 0.5 - 1.0 amp range, i.e. an order of magnitude greater than in Series A. A black deposit began to appear after about a day's operation. Smooth operation was observed all the way to dryness, i.e. steady current, falling rapidly to zero at dryness.

Series C

This series was initiated to determine whether appearance of the black deposit was related to the nature of the pre-treatment of the electrodes.

Cell: Small glass vials, with electrodes:

(1) 304 stainless steel screen, degreased

(2) As (1), followed by HNO_3 wash.

(3) As (2), followed by HF pickling.

(4) 304 stainless shim stock, degreased only.

Wick: None

Electrolyte: 5% dihydrazinium oxalate

Potential: 2-3 volts

Results: All gave some discoloration indicative of corrosion. It was apparent that pre-treatment of the electrodes was not a factor in corrosion.

Series D

The objective of this series was to determine the threshold voltage for corrosion of stainless steel electrodes.

Cell: As in C

Wick: None

Electrolyte: 5% dihydrazinium oxalate

Potential: 2.4 - 6.5 volts

Result: Some corrosion was observed during the first day of electrolysis.

Because the above experiments, carried out at potentials of two or more volts, showed corrosion of stainless steel anodes and partial replating of the dissolved metal as a black, amorphous, non-adherent deposition on or near the cathode, approximate threshold voltages for electrolysis were determined for stainless steel and nobler metals, with the results tabulated below.

Metal	Electrolysis Threshold Voltage
Stainless	0.4 - 1.4
Gold	1.4
Platinum	0.5

Corrosion was observed at the threshold voltage in all cases. The corrosion was qualitatively less for the gold and platinum. In search for a new anode material, carbon electrodes were then removed from several ordinary dry cells. These electrodes functioned well at several volts without obvious corrosion. Threshold voltage was 0.5 to 0.7 volts. There was, however, considerable mechanical attrition on operation at high current densities, apparently caused by gas bubble formation in the rather porous surface layer.

Graphite spectrograph electrodes were much better. In a cell with two 1/4 inch diameter rods immersed to a depth of about 1 inch, a 0.2% oxalate solution was electrolyzed at 28 volts. The current was large, a maximum of 1.15 amperes during the time it took to electrolyze completely to dryness. No abnormalities were observed and the electrodes were in good condition at the end of the experiment; only a few milligrams of material was lost by attrition even though graphite is easily abraded.

A second cell was assembled with a carbon rod anode and 304 S.S. cathode. With a reduced electrolyte concentration of 0.05% the cell operated at an equilibrium current of about 300 ma and was also successfully run to dryness. The stainless cathode showed no evidence of discoloration and the anode was intact.

Following the encouraging results with graphite, a number of graphite and carbon materials were evaluated, including:

Material Designation	Description
EH	Soft Graphite
3499	Medium Hard Graphite
9429	Hard Graphite
580	Spectroscopic Grade Graphite
9139-PCI	Pyrolytic Carbon Impregnated Graphite
9326	Very fine grained graphite
890	Carbon

All of the above materials are molded, which should provide greater resistance to shedding of particles during electrolysis than the extruded materials. The tests completed are summarized in Table IV. Test conditions were:

Electrodes tested: 2 pairs of EH graphite (soft)
1 pair of 3499 graphite (medium hard)
1 pair of 9429 graphite (hard)

Electrolyte: None

Potential: 14 volts

Temperature: 20°C (68°F)

Test Duration: 5 days

TABLE VI EVALUATION OF GRAPHITE ELECTRODES

Type of graphite (Speer designation) and relative hardness	Polarity of Electrode	Weight Change*
EH (soft)	+	+5.2 mg
EH	-	+0.9
EH	+	+13.1
EH	-	+1.3
3499 (Medium Hard)	+	+6.4
3499	-	+3.8
9429 (Hard)	+	-0.2
9429	-	-0.9

* Total weight immersed electrodes about 1.1 gram.

Visual examination at the end of the test showed no indicating of electrode attack. The weight changes of the electrodes were very small and did not indicate weight loss for the anodes, as would be expected if electrode attack had occurred. The small weight gains are in most cases within the errors of measurement. It is possible that some weight gain may be due to absorbed hydrazine which was not removed by the 24 hour baking period in a vacuum oven prior to final weighting.

As a result of the electrode investigations, graphite anodes and either 304 stainless steel or aluminum cathodes will be employed in Task V.

V. Power Requirements

Any propulsion system which requires electrical energy for operation may, as a result, suffer a weight penalty. It is appropriate to analyze the hydrazine electrolysis power requirements in terms of the specific mission under consideration.

As mentioned previously, under practically all conditions, hydrazine is electrolyzed directly to the elements:

$$N_2H_4 + 4 \text{ Faradays} \longrightarrow N_2 + 2H_2$$

On converting Faradays per mol to ampere-hour per pound, it is found that the requirement is 1521 amp-hour/lb or, in terms of useful total impulse:

$$\frac{1521 \text{ amp-hrs/lb}}{125 \text{ sec.}} = 12.2 \text{ amp-hrs/lb-sec.}$$

This may be interpreted in terms of the requirements of the mission. The original mission profile allocated the following total impulse for cruise mode (the only requirement for gas thrust with the dual mode hydrazine system):

	1600 lb-sec.	cruise attitude control
	140 lb-sec.	gas leakage
	230 lb-sec.	share of cross coupling in 3600 lb-sec. system
	10 lb-sec.	residual gas at end of mission
Total	1980 lb-sec.	

The allocation for residual gas was based on a liquid volume of 3.22 liters of propellant consumed by the catalytic engines which must be replaced by an equal volume of gas at a minimum system pressure of 90 psia.

$$\frac{6.12 \text{ atm} \times 3.22 \ \ell}{.08205 \times 298^{\circ}K} \times \frac{32g}{\text{Mol}} \times \frac{1 \text{ lb}}{454 \text{ g}} \times \frac{125 \text{ lb-sec.}}{\text{lb}} = 7 \text{ lb-sec.}$$

This calculation is based on the 3600 total lb-sec. system. The larger 5200 lb-sec system would require a slightly larger volume (an additional 3.16 liters). A nominal allocation of 10 lb-sec. applies to either system within the accuracy of the following calculation.

For a total mission time of 9720 hours the continuous current is calculated as

$$\frac{12.2 \text{ amp-hrs/lb sec.} \times 1980 \text{ lb-sec.}}{9720 \text{ hours}} = 2.49 \text{ amps continuous}$$

The above requirement was based on the allocation made originally for Ranger and Mariner. Performance of the latter two spacecraft has indicated the allocation was conservative and an assumption of one impulse bit in each axis every half-hour might be more nearly correct. In that case, for 4 thrusters firing simultaneously in each of three axes with an impulse bit each of 1.6×10^{-3} lb-sec., the total requirement for a 9720 hour mission is:

$$9720 \times 4 \times 3 \times 2 \times 1.6 \times 10^{-3} = 373 \text{ lb-sec.}$$

Then the total for the mission would be:

	373 lb-sec.	cruise attitude control
	140 lb-sec.	gas leakage
	30 lb-sec.	share of cross coupling
	10 lb-sec.	residual gas
Total	543 lb-sec.	

$$\frac{12.2 \text{ amp hours/lb sec.} \times 543 \text{ lb-sec.}}{9720 \text{ hours}} = 0.68 \text{ ampere, continuous}$$

Actually, the latter requirement is also thought to be conservative since it is likely that Mariner did not limit cycle as often as every half hour (based on gas supply and mission duration). Further, future spacecraft may well have more sophisticated control logic which will allow further reduction in impulse.

The power consumption rate depends on the voltage at which the cell is operated. Since it has been shown that a given cell may be operated at ordinary spacecraft bus voltage as well as the minimum voltage required for electrolysis, more than one operating mode must be considered.

Three possible voltages are considered here:

(1) One volt -- the probable lowest desirable voltage

(2) Two volts -- conservative low voltage operation

(3) Twenty-eight volts - nominal bus voltage.

The power required is shown in Table VII.

TABLE VII

Continuous Power for Space

Probe Mission

Mission	Watts Continuous Power		
	1V	2V	28V
Very conservative 1980 lb-sec. (from original mission)	2.5	5	70
Conservative 543 lb-sec. (from later estimate).	0.7	1.3	19

It should be noted that increasing voltage above the minimum required to initiate electrolysis is not of direct benefit inasmuch as gas production is related only to the current passed. Any excess voltage (over about 0.5 - 0.75V) appears as an ordinary ohmic drop and the power is dissipated as heat. This heat has not proved to be troublesome in our work to date.

Operating directly from unregulated spacecraft voltage does have the advantage that no power conditioning equipment is required and the system will be somewhat simpler and more reliable. The power shown in Table VII for 28 V is appreciable, although perhaps tolerable in a large spacecraft. Also, as noted above, mission requirements may prove to be less than the present estimate.

Operation at other than bus voltage requires DC to DC power conversion. This may be accomplished by lightweight and quite reliable solid-state devices. One volt should be acceptable since no noticeable current decay with time has been noted in the experimental work to date. Two volts, however, would allow an additional margin of safety with little additional power loss.

It will be the goal of the Task V investigation to make a cell which will operate equally well throughout the indicated range.

VI Wicking Materials

Under low or zero-g conditions, it is necessary to provide means to assure contact of the electrode surfaces with the hydrazine. The most obvious technique is by means of a wick. For the mission under consideration, the rate of fluid transport only need by very small (of the order of 0.15 g/hr. for four thrusters acting simultaneously in each of three axes twice per hour, with each thruster delivering 1.6×10^{-3} lb-sec. total impulse), so highly efficient wicking action is not mandatory. Faster wicking may be required for other mission, however, so one criterion for selecting a wick is reasonably rapid action. In addition, it is desirable to have a material which is consistent in its properties and whose composition is well controlled. A wick must have physical properties such that it does not contaminate the propellant with solid matter. Any fibrous wick may be expected to generate undesirable contamination by mechanical attrition of fine particles. This is not thought to be a severe problem, for the final design may include a fine mesh screen sheath for the wick which will exclude particles from the main tank.

The use of fiber optic strands for wicking was considered; it was concluded that this approach is not particularly promising. Such fibers are composed of two different types of glasses in a core and sheath coaxial form. The two different glasses, usually a borosilicate and a barium flint glass, are selected solely on the basis of index of refraction and not for improved physical properties. Consequently, the unique construction of the fiber optic is thought not to possess any particular advantage over a homogeneous glass filament. Also, it is doubtful that better wicking would be realized. An aligned bundle of parallel fibers might be more efficient than random or woven fibers in the longitudinal direction, but would probably be inferior in the transverse direction.

A number of kinds of materials were tested, including glass cloths and batting, glass fiber papers, asbestos filtersand felts, carbon cloths, and felts made from synthetic fibers. One alternative, not investigated to date, is a porous ceramic wick.

The experiments indicated that commercially available glass cloth materials are probably the most suitable for wicking in the dual hydrazine system. The cloth does not wick as fast as the glass fiber paper and glass felts, but has much better structural integrity.

A number of samples of glass cloth were examined. These were essentially pure silica material prepared by leaching of glass fibers to remove all other components and leave a porous structure. The only remaining question concerning these wicking materials was their compatibility with hydrazine. The results of such investigations are given under Compatibility (Section VIII below).

VII Controllability of Hydrazine Electrolysis

A. Stoichiometry and Thermodynamics of Electrolysis

The decomposition of hydrazine is an exothermic process, and accordingly there is concern that at high electrolysis rates enough heat might be generated to cause a self-sustaining thermal decomposition. As discussed above, the evidence is that the stoichiometry of electrolysis of neat hydrazine is:

$$N_2H_4\ (\ell) = N_2(g) + 2H_2(g);\ \Delta H^\circ_{298} = -12.10\ \text{kcal}$$

The heat from this reaction will necessarily be to some extent dissipated by heating and vaporization of the undecomposed reactant:

$$N_2H_4\ (\ell) = N_2H_4\ (g);\ \Delta H^\circ_{298} = 10.69\ \text{kcal}$$

If thermal equilibration occurs, then, the hydrazine will be vaporized, and since the gas cannot be electrolyzed, the electrolysis process is self-limiting in normal operation, and the temperature of the hydrazine could not rise above the boiling point.

Normal operation of the electrolysis cell would likely not involve much heating from electrolysis, because the amount of liquid electrolysis required for propulsion is very small compared with the total amount of propellant present. The abnormal circumstances which must be considered include shorting of the electrodes such as by means of a loose wire bridge between electrodes. In such a case, if there were transient retention of the hydrazine vapor in the vicinity of the electric current, it is conceivable that superheating of the vapor would take place.

The composition of the gas generated by electrolysis and vaporization is of interest, for the greater the dilution of the N_2H_4 (g) by the decomposition products the more inhibited will be the decomposition of that entity. The greatest amount of gaseous hydrazine will be formed if through malfunction or for other reason the electrolysis should be continued to dryness. The composition of the gas mixture formed may be estimated by a simple thermodynamic calculation for the process:

$$N_2H_4\ (\ell,\ 298^\circ K) \rightarrow (1 - X)\ N_2H_4\ (g,\ T) + X N_2\ (g,\ T) + 2X\ H_2\ (g,\ T),$$

where T is the boiling point and X is the fraction decomposed. If the process is adiabatic, the ΔH for the above reaction may be equated to zero, and hence:

$$X = \frac{10.69 + (H_T - H_{298})^{N_2H_4(g)}}{\Delta Hf_T\ N_2H_4(g)}$$

From this equation and the JANAF Thermochemical Tables (24), it is found that at the normal boiling point (113.5°C) the gas formed will be about 20% N_2H_4 (g); at 500°K (440°F) it is 16% N_2H_4 (g).

It follows, then, that an explosive decomposition of hydrazine under electrolysis conditions is unlikely for several reasons:

(1) In normal operation, the electrolysis is inherently self-limiting because of the highly endothermic vaporization.

(2) The hydrazine vapor generated by heating from the electrolysis is necessarily diluted with significant quantities of non-reactive decomposition gases.

(3) In spacecraft application, only very small amounts of liquid need be electrolyzed at any given time.

(4) The pressure levels in the tank will be governed by the operational requirements of the catalytic thrusters, and need not be more than a few hundred psi. The boiling point of the liquid accordingly will probably not be high enough to initiate autodecomposition.

B. Experimental Testing of Controllability

Although the thermodynamic calculations are encouraging, the only reliable evidence of controllability must come from experiments. Accordingly, a series of laboratory glassware and high pressure bomb tests have been conducted.

1. Laboratory Glassware Tests

Two series of tests were conducted. The first, short-duration runs, were carried out in small cells formed from rectangular metal screens immersed in the liquid; the second series involved longer duration runs in cells provided with wicks. The fundamental problem investigated was the possibility of malfunctions leading to the production of hot spots, which might result in explosive decomposition. In the short term tests, severe heating was engendered by small (3 mil diameter) wires between the electrodes, thus simulating a failure of the cell due to shorting by a small piece of metal. In the longer duration tests, cells with wicks were allowed to operate under adverse conditions (such as shorted electrodes) for periods of several days.

A summary of these tests is presented in Table VIII; a more complete description is presented below.

a. Short Duration Tests

Experiment 1 - (Water Electrolysis, Shorted Cell)

An 18-8 stainless steel wire of 3.0 mil (0.075 mm) diameter was connected across the electrodes of a small cell formed from

TABLE VIII

SUMMARY OF PRELIMINARY "HOT SPOT" TESTS

Experiment	Solvent	Short	E	I	t	Wick	Result
1	H_2O	Wire	Up to 3V	0.9 Amp		None	Boiling and Burnout
2	N_2H_4 N_2 Atmos.	Wire	Up to 7.0V	3.0 Amp	3-5 sec.	None	No burnout in 3 trials
3	N_2H_4 Air Present?	Wire	4.0V 6.5V	1.4 Amp 2.5 Amp	60 secs. 7 Minutes	None None	Hydrazine Heated Strong Heatings; Flame when wire no longer in liquid.
4	N_2H_4	None	20V	1.9-1.0 Amp	35 mins.	None	Boiling; No Failure
5	N_2H_4	Wire	Up to 2.4V	Up to 2.5 Amp (@ b-o)	A Few Minutes	None	Burnout; No Failure
6	N_2H_4	Wire	Up to 4.1V	Up to 2.15 Amp	A Few Minutes	Glass Cloth	Burnout; No Failure
7	N_2H_4 - $N_2H_5NO_3$ N_2 Purge	None Intended	1.0V	20-300 ma	4 days	Glass Cloth	Fire; Corrosion may have shorted cell
8	N_2H_4 - $N_2H_5NO_3$ N_2 Purge	None Intended	4.0V	0.75 Amp	10 days	Glass Fiber Paper	Probably Shorted; Corrosion

2.0 cm x 5.0 cm (0.8 in x 2 in) rectangular screens of 24 mesh 304 stainless steel. Electrode separation was 8 mm (0.3 inches). The cell was immsered in water and the voltage across the electrodes was increased slowly until the wires burned out. Violent boiling of the water near the hot wire was observed, with burnout occurring at approximately 0.9 amperes and 3 volts in each of three trials.

Experiment 2 - (Hydrazine, Shorted Cell)

The shorted cell described above was immersed in anhydrous hydrazine in an inert atmosphere of nitrogen and electrical power was applied for periods of 3 to 5 seconds. Burnout did not occur during 3 trials at voltages of up to 7.0 volts, which gave currents of about 3.0 amperes. Violent boiling and vigorous electrolysis were observed during the trials at the higher voltages.

Experiment 3 - (Hydrazine, Shorted Cell)

The shorted cell employed in experiment 1and 2 above was allowed to operate at 6.5 volts until failure occurred. In a preliminary trial, the cell was operated at 4.0 volts for 60 seconds, which heated the hydrazine but did not burn out the wire. Then a thermocouple was placed in the container, the hydrazine was replaced with fresh hydrazine, and the test was continued. Most of the test was carried out at 6.5 volts, which gave a current of 2.5 amperes. The hydrazine was heated to boiling and continued to boil very vigorously for several minutes, with hydrazine being lost by evaporation and by escape of the frothy boiling liquid through holes in the top of the cell container. Approximately 7 minutes after the beginning of the second trial, the liquid level appeared to reach approximately the level of the 3 mil wire. A hydrazine decomposition flame was initiated at this time, which consumed the remaining hydrazine. The heat generated by the burning hydrazine was sufficient to melt the polyethylene cap of the vial and to cause the vial to crack from thermal stress. The burning was probably initiated by increasingly poor heat transfer from the electrically heated wire, which allowed the wire to reach increasingly higher temperatures before quenching with liquid hydrazine occurred. It is possible also that a small amount of air inadvertently entered the test chamber, contributing to the ignition of the hydrazine.

Experiment 4 (Hydrazine, Non-Shorted Cell)

A vial of hydrazine was electrolyzed at a high current density for 35 minutes. The electrolysis cell was similar to those described above, except that the electrodes were not shorted by a fine wire, and the electrode spacing was reduced to 4 mm. The cell voltage was set at 20 volts, and the amperage dropped from an initial value of 1.9 amperes to a final value of 1.0 amperes as the hydrazine

liquid was removed from the cell. Sufficient heat was liberated during the electrolysis to maintain a vigorous boiling of the hydrazine. The current density of the cell is estimated to have increased during the electrolysis from an initial value of about 380 ma cm^{-2} to a final value of about 500 ma cm^{-2}, based upon estimated immersed cell areas of 5 cm^{-2} initially and 2 cm^2 at the end of the electrolysis. No adverse effect other than the boiling of the hydrazine appeared to result from the high current density imposed upon the cell.

Experiment 5 - (Hydrazine, Shorted Cell)

A cell similar to that employed in experiment 4 above was shorted by a 3 mil (0.075 mm) wire. The voltage was increased slowly until wire burnout, at a voltage of 2.4 volts and a current of 2.5 amperes. No other effects were noted as a result of the burnout; the only indication of burnout was a sudden drop in the amperage at the applied voltage. Examination of the wire showed fusion of the ends of the parted section of wire.

Experiment 6 - (Hydrazine, Shorted Cell)

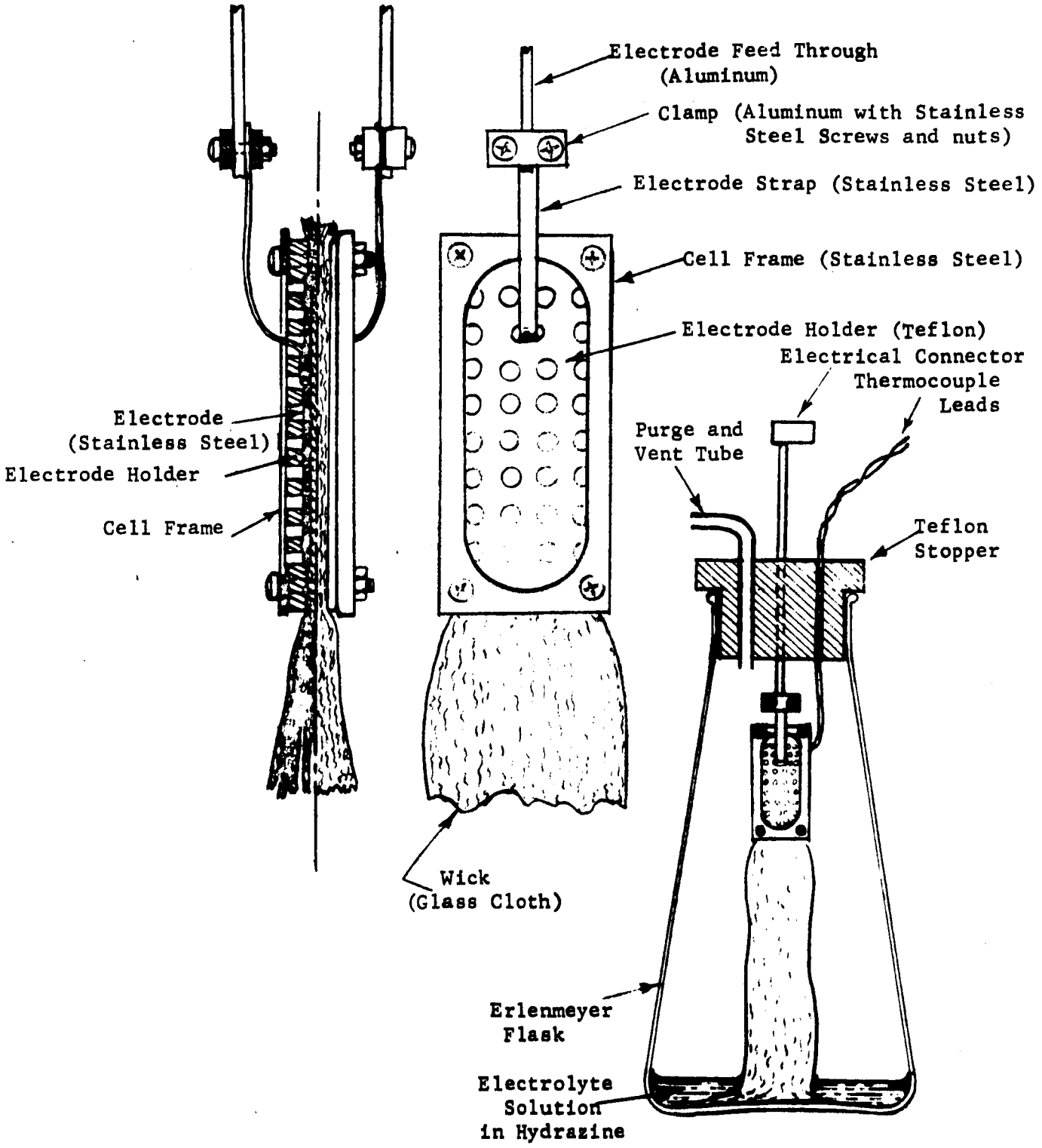
A cell similar to that employed in experiment 5 above was provided with a glass coth wick formed from 9 layers of glass cloth. The electrodes were shorted by passing a 3 mil stainless Steel wire through the electrodes and wick at a point about 1 cm above the bottom of the cell. The cell was immersed in hydrazine to a level about 1 cm above the location of the shorting wire. The voltage across the cell was increased slowly until the shorting wire burned out. Burnout occurred at a voltage of 4.1 volts and a current of 2.15 amperes. The only indication of burnout of the wire was the sudden drop in amperage.

b. Long Duration Tests

Experiment 7 - (Hydrazine - Hydrazine Nitrate, Probably-Shorted Cell)

A cell with 2.0 x 5.0 cm electrodes similar to those described above was constructed for operation in a closed flask. The experimental apparatus is illustrated in Figure 3. The cell was operated on a hydrazine nitrate solution in hydrazine with an initial concentration of 2.0% for a period of 4 days. A slow nitrogen purge was maintained through the flask to preclude the entrance of air into the cell. The cell was operated at 10 volts to provide a relatively severe operating condition.

A rapid increase in cell current (from about 20 ma to 300 ma) was noted near the end of the second day of operation. On the fourth day of operation a fire apparently occurred which consumed the remaining hydrazine and generated enough heat to crack the flask at the lip. Pressure buildup in the flask apparently was negli-



EXPERIMENTAL ELECTROLYSIS APPARATUS

FIGURE 3

gible; the Teflon stopper was not dislodged. There were no records of the operating parameters of the cell at the time of the fire because instrumentation was not available at that time.

Disassembly of the cell revealed extensive deposits of corrosion products on the electrodes and in the wick in a relatively small area at the top of the cell.

Because of the lack of instrumentation records at the time of the fire, few conclusions can be drawn concerning the cause of the fire. From the rapid increase in cell current observed in the second day of operation and the localized corrosion, it appears likely that a short circuit developed in the cell and resulted in local heating. The corrosion probably was enhanced by a combination of the temperature increase and high concentrations of hydrazine nitrate caused by the vaporization of hydrazine in the vicinity of the short circuit. The minimal nature of the damage caused by the fire seems to indicate that little hydrazine remained in the flask at the time of the fire.

Experiment 8 - (Hydrazine - Hydrazine Nitrate, Cell Probably Shorted)

During the period in which Experiment 7 was running, an improved cell of similar design was fabricated and instrumentation for the recording of cell voltage, amperage, and temperature was developed. Improvements in the apparatus included the elimination of several aluminum alloy parts from the cell; all metal parts exposed to the hydrazine were fabricated from stainless steel. An improved Teflon electrode holder and stainless steel frame were fabricated. The wick employed in the cell was fabricated from the glass fiber paper material supplied by Strathmore Paper Company.

A 24-point Bristol recorder was employed to provide either continuous recording of the cell performance or sampling of the data at 15 minute intervals. Modification of the recorder resulted in 10 channels of direct millivolt recording and 14 channels of thermocouple recording. The recorder was not available until the middle of Experiment 8.

The cell was operated at 4.0 volts for 10 days with an electrolysis solution of 1.7% hydrazine nitrate in hydrazine. It was found that the current remained essentially constant at its initial value of 0.75 amperes throughout this time, which indicated that a short circuit of the electrodes probably had occurred prior to the start of the test. The test was allowed to continue until the area of corrosion because visible at one corner of the electrode and wick. The cell was then disassembled and examined.

It was found that the area of corrosion centered about one corner of the electrode screens and that both anode and cathode appeared to be equally involved. The wick at the eroded corner of the electrodes was very thin and was heavily loaded with corrosion products. It was concluded that a short circuit of the cell had occurred at the corner of the cell, and that the corrosion observed in this area had been promoted by the resulting hot spot.

c. Conclusions:

Two of the above tests resulted in fires, but no detonations. The first (Experiment 3) involved a deliberately short circuited cell which was run until the liquid level fell below the shorting wire. The wire became red hot when no longer cooled by liquid heat transfer and ignited the vapor from the boiling hydrazine. Ignition may have been aided by the presence of air in this particular experiment.

The second fire (Experiment 7) occurred during vigorous electrolysis of hydrazine containing hydrazine nitrate electrolyte. At the time of the fire the solution was approaching dryness and a short circuit was suspected. Corrosion on a portion of the electrodes supports the contention of overheating of a local area where hydrazine nitrate was concentrated. This test indicated that hydrazine nitrate may cause a problem under some circumstances and, while not precluded as an electrolyte, would require caution in usage.

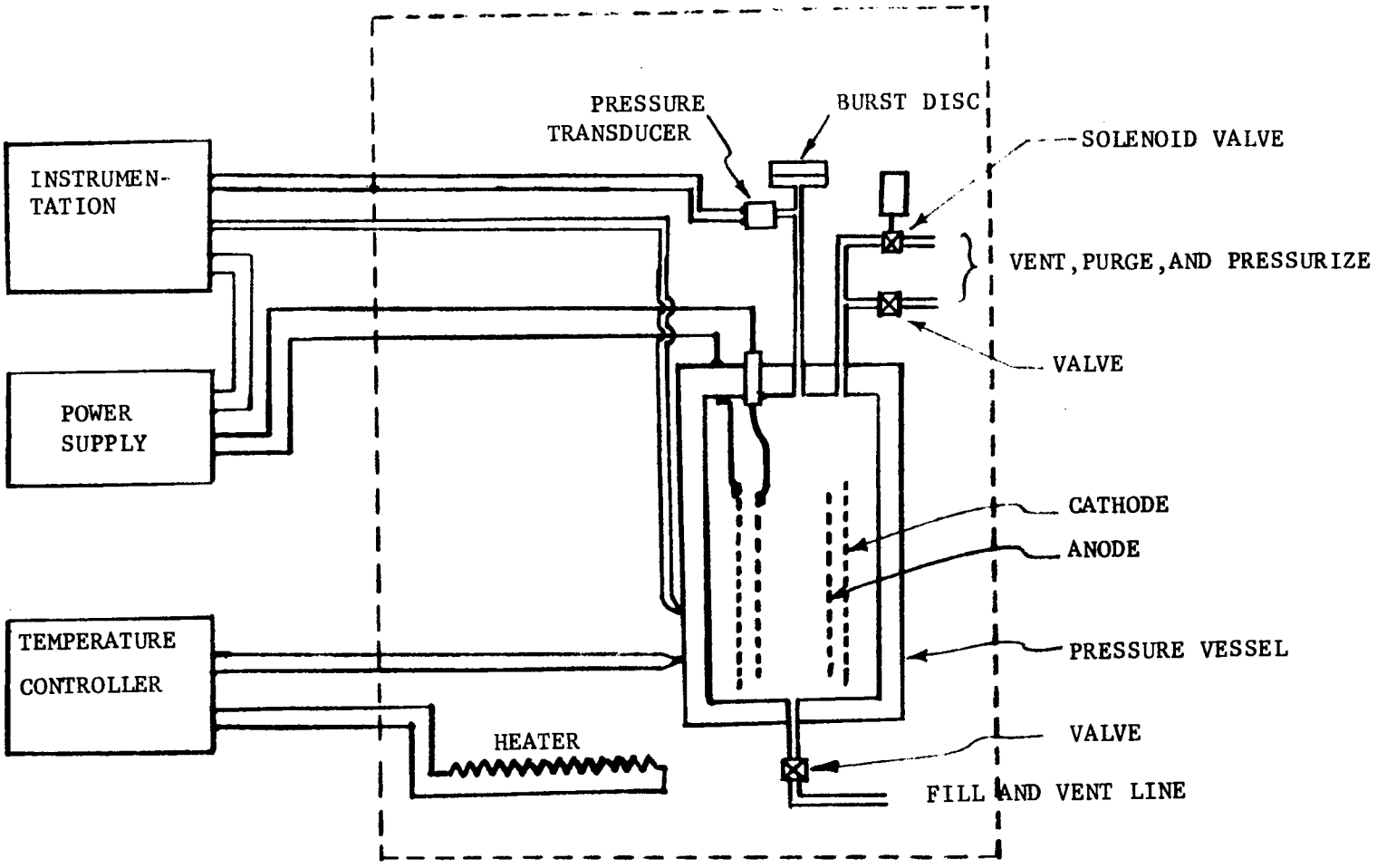
The laboratory glassware tests thus gave no cause for serious alarm concern reaction controllability. They were followed by bomb tests with hydrazine oxalate electrolyte, with exclusion of air.

1. High Pressure Bomb Tests

A bomb assembly, as shown in Figure 4, was constructed to demonstrate controllability under conditions of high pressures and temperatures. It consisted of a heavy-walled stainless steel bomb containing the electrode assembly, a thermostatically controlled enclosure for the bomb, a D.C. power supply, and instrumentation for recording the cell temperature, pressure, voltage, and current.

The first experiment with this apparatus was conducted with 304 stainless steel screen anode and cathode. At the time of this test it was recognized that corrosion might be a problem so the voltage was maintained only slightly over the electrolysis threshold. Concentric cylindrical electrodes fabricated from Type 304 stainless steel screens were employed. The temperature was maintained from 40°C (104°F). A hydrazinium oxalate solution containing 3.24% by weight oxalic acid was electrolyzed for one week at approximately 1 volt.

It was found that the pressurization of the bomb proceeded smoothly and that the rate of pressurization was approximately proportional to the cell current. (See Figure 5). The test was terminated, because of the limitation of the burst disc, when the pressure reached approximately 600 psig.



MATERIALS:
All stainless steel and Teflon (except gold feed-through)
Electrodes: 304 Stainless Steel

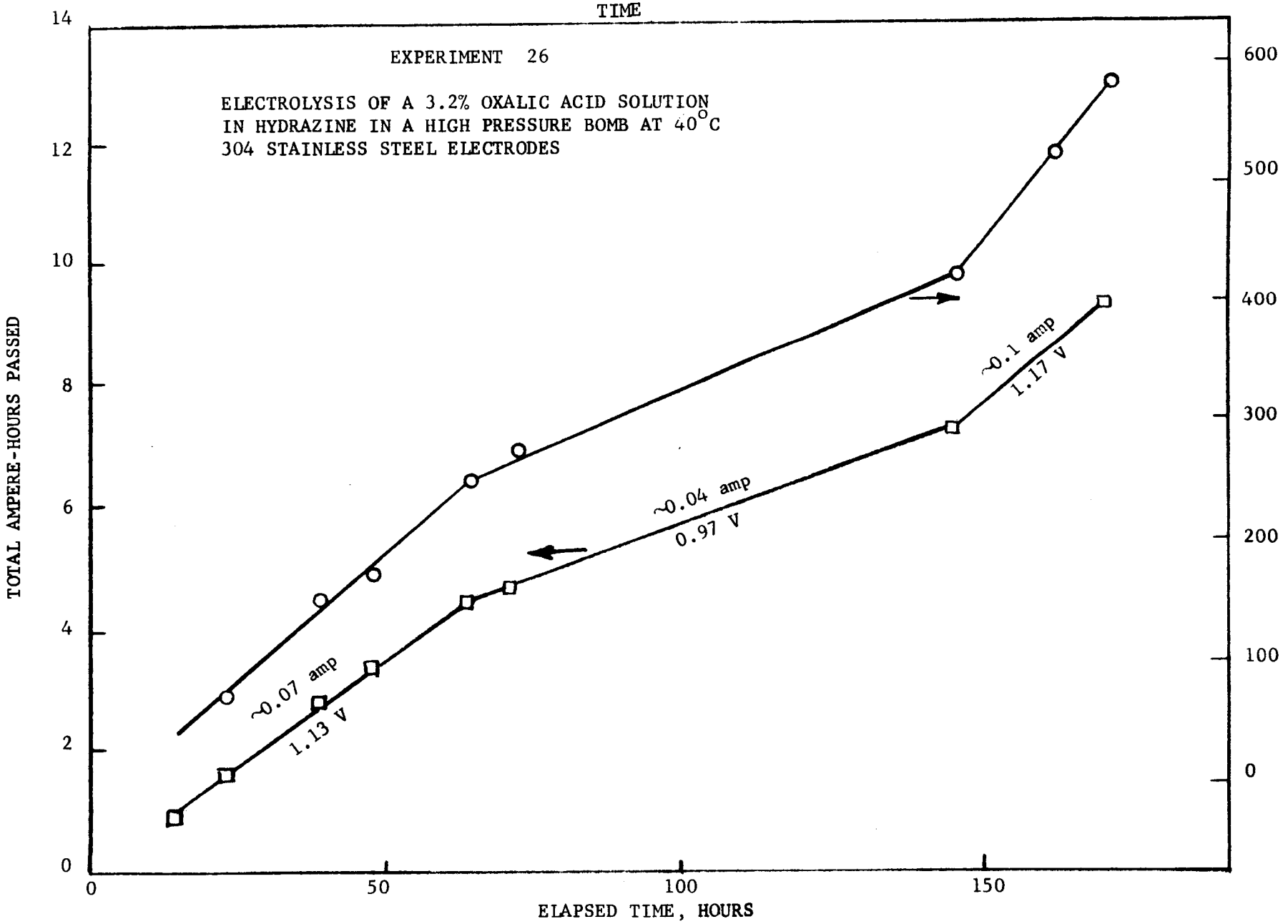
PARAMETERS RECORDED:
Cell Current
Cell Voltage
Pressure
Temperature

FIGURE 4

HIGH PRESSURE ELECTROLYSIS TEST CELL

FIGURE 5

AMPERE-HOURS AND PRESSURE VS TIME



Inspection of the bomb contents after the test revealed that some transport of the electrode material had occurred. The cathode was coated over the area in closest proximity to the anode with a black deposit which weighted approximately 100 mg. A faint darkening of the inner wall of the pressure vessel, which was at the same potential as the cathode, was also observed. The hydrazine removed from the bomb was pale reddish in color.

As a result of the experience in the first test, further work was conducted with graphite anodes (Grafgard Electrodes Company, El Monte, California, 0.242 inch diameter electrodes for spectrographic analysis.) Runs at 2 volts to 27.7 volts and at concentrations of oxalate from 0 to 1.0% (expressed as oxalic acid) gave cell currents between 0.56 and 1.1 amperes. All tests were at a nominal 40°F (104°F). The results are summarized in Table IX in Figures 6 and 7. The conclusions were:

a. No indication of uncontrolled reaction has been found at voltages up to 27.7 volts and with cell currents as high as 1.1 amperes. The rate of pressure increase with time is qualitatively proportional to electrolysis current (Figure 6). In one case (Experiment 47) it was found on termination of the experiment that the calibration of the pressure transducer had shifted. Since the dashed segments of the curve for experiment 47 have the same slope at the curve prior to the first break, and since this slope (at cell current = 0.97 amperes) is in the expected relationship to the slope of the curve for experiment 45 (cell current = 1.0 ampere), it is concluded that the breaks in the curve resulted from instrumentation difficulties.

Another problem in experiment 47 was failure of the temperature control, with the result that the cell temperature reached a maximum of approximately 80°C (176°F). This inadvertent rise in temperature without ill effect is in itself useful evidence of controllability.

b. No visual evidence of corrosion of the graphite anode or cathode has been found, and electrode weight losses or gains have not exceeded 2.6 mg (out of about 1.2 grams) in any high pressure experiment.

c. The variation of cell current with voltage, as shown in Figure 7, gives the expected increase in cell current with increasing electrolyte concentration. A threshold voltage somewhat less than 1 volt is also evident. It is interesting to note that initial hydrazine conductivity is quite sensitive to storage and handling. The conductivity of hydrazine in Experiment 47 (before addition of electrolyte), as shown in Figure 7, is considerably greater than that of Experiment 42. The hydrazine of Experiment 47 had been stored in a clean, well-stoppered glass bottle for about two months. However, when approximately 0.5% oxalic acid was added, conductivity of both samples of hydrazine was nearly identical (cf. Experiment 47 and 48). It is concluded that initial conductivity is ordinarily small and differences, although easily discernible, are essentially eliminated by addition of small amounts of electrolyte.

TABLE IX SUMMARY OF HIGH PRESSURE ELECTROLYSIS CELL TESTS

Experiment No.	26	42	45	47	48	49
	Anode: 304 CRES Cathode: 304 CRES	Anode: Graphite Cathode: 304 CRES	Anode: Graphite Cathode: 304 CRES	Anode: Graphite Cathode: 304 CRES	Anode: Graphite Cathode: 304 CRES	Anode: Graphite Cathode: Aluminum
Electrolyte	3.2% oxalic acid	None added	0.03% oxalic acid	1.0% oxalic acid	0.5% oxalic acid	0.5% oxalic acid
Electrolysis Conditions	E between 0.97 & 1.14V I between 0.035 & 0.100A T = 104°F	E = 27.7V I between 0.5 and 0.8A T = 104°F	E = 14.5 V I $\simeq$ 1A T = 104°F	E = 2.0 to 2.5V I = 0.92 to 0.95A T = 104°F	E = 3-4V I = 1 amp T = 40°V (104°F)	E = 2-2.5V I = 0.33 amp T = 55°F
Duration	153 hours	Trial A: 47.2 hrs Trial B: 50.5 hrs	47.3 Hours	26.8 Hours		101 hours
Results	Corrosion observed, deposit on cathode weighs 107 mg; hydrazine solution is pale reddish color	No corrosion observed; electrode weight changes are neglible	No corrosion observed; electrode weight change are negligible	No corrosion observed; electrode weight changes are negligible	No corrosion observed; electrode weight changes are negligible	No corrosion observed
Estimated Efficiency	*ϵ = 93% at 0.97V = 112% at 1.14V	ϵ_A = 83% $\pm$ 8%	ϵ = 99.6% ϵ_B = 76 $\pm$ 5%	ϵ = 90.7%		ϵ = 87%

*ϵ = efficiency = $\frac{\text{observed rate of pressure rise}}{\text{calculated rate of pressure rise}}$

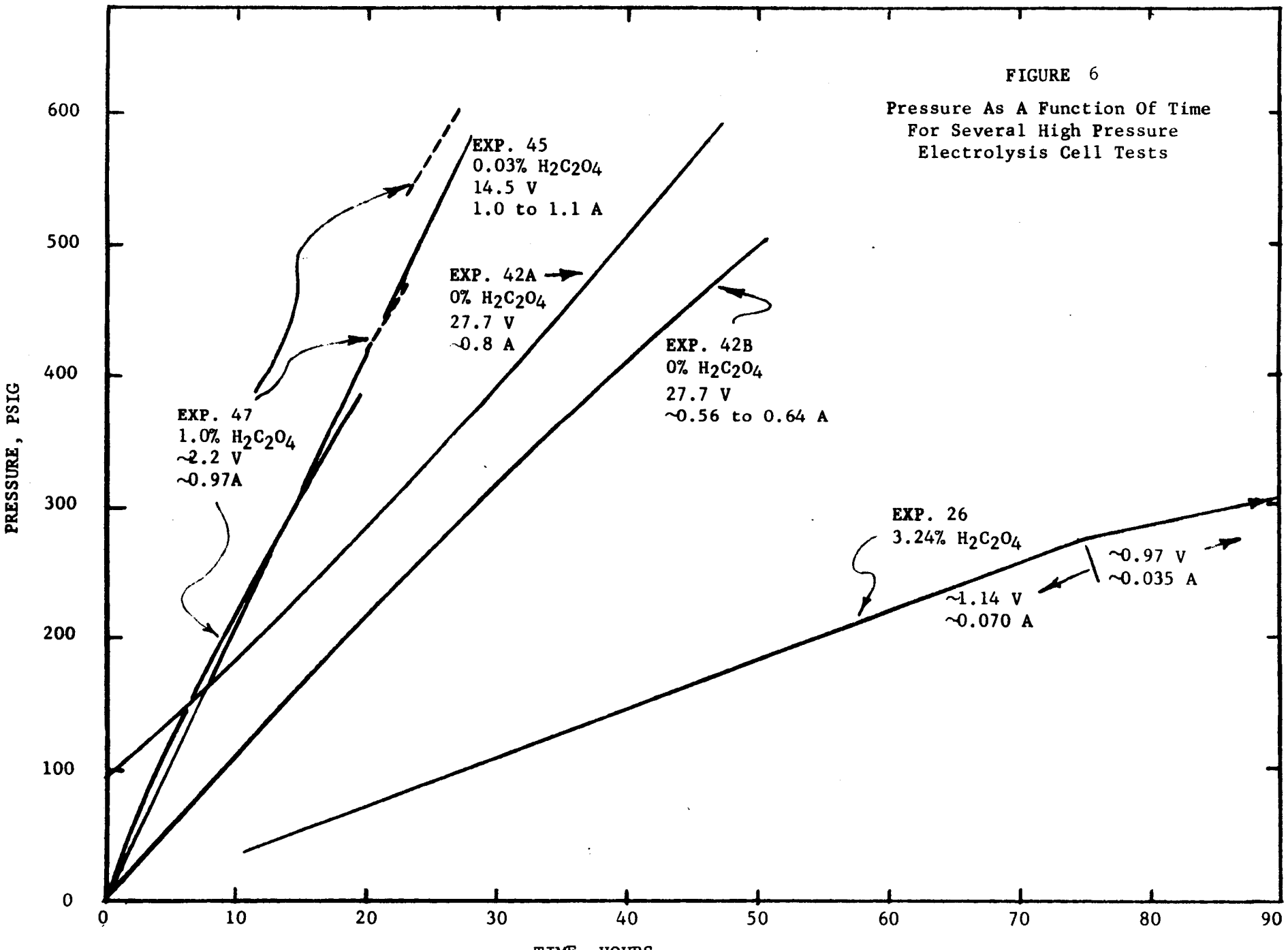


FIGURE 6

Pressure As A Function Of Time
For Several High Pressure
Electrolysis Cell Tests

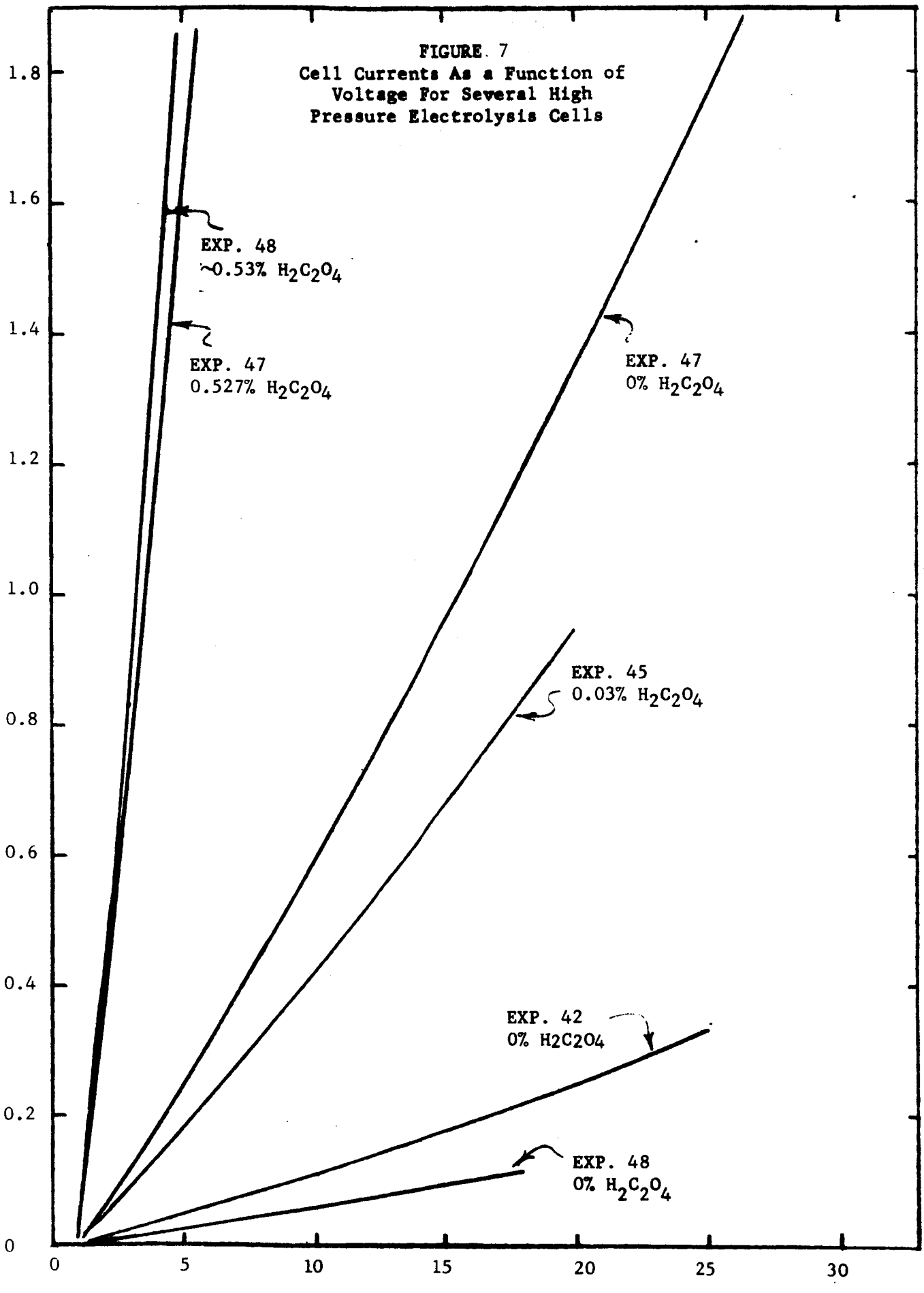


FIGURE 7
Cell Currents As a Function of Voltage For Several High Pressure Electrolysis Cells

d. Table IX shows the estimated current efficiencies, θ, computed by comparing the observed pressure rise rate with the pressure rise rate calculated by assuming the reaction

$$4 \text{ Faradays} + N_2H_4 \longrightarrow N_2 + 2H_2$$

Theoretical efficiencies between 75.7% and 122% were found, but an analysis of the errors in the calculation has indicated that a rather large variation in θ might be anticipated. The principal sources of error are considered to be:

(1) Leakage of gas from the apparatus.

(2) Reading of the pressure, cell current, and elapsed time from the recorder chart.

(3) Uncertainties in the solubilities in hydrazine of the generated gases.

(4) Instrumentation.

e. Additional investigations, which can be conducted as part of Task V, include elevated temperature runs and more accurate measurements of cell efficiency. The simplest method for obtaining accurate measurements of the total current passed through the electrolysis cell will be the introduction of a coulometer in series with the cell. Refinement of the pressure transducer readout will provide pressure rise rate data of higher accuracy. Measurements of temperature and time can easily be made to suitable accuracy. A remaining source of error is the accuracy of the solubility data for hydrogen and nitrogen in hydrazine at the temperatures and pressures of interest; accurate efficiency measurements might be of use in evaluating the reported data.

VIII Compatibility

The electrodes, wicks, and materials of construction of the electrolysis cell must be compatible with the hydrazine solution being electrolyzed. Almost no information is available on the compatibility with the materials of interest of dilute hydrazinium oxalate solutions in hydrazine; some data may be found for hydrazinium nitrate solutions. A considerable amount of data has been accumulated on hydrazine propellant compatibilities by various aerospace organizations. These data will be reviewed and some experiments conducted on the contract will be described.

Two essential problems must be considered: catalytic decomposition of the hydrazine, and corrosion or chemical attack on the substrate. In both cases, the interpretation of the data is subject to qualification because of random or external factors which may predominate. Gas evolution rates are especially sensitive to trace contamination, making it very difficult to categorize a material as incompatible unless the gas evolution rate is substantially greater than the controls.

The latter problem may be illustrated by the recent results from JPL (Reference 25). In brief, the referenced experiments were conducted by sealing test specimens in Pyrex ampoules which were connected to a stainless steel pressure gage through a Kovar seal and Swagelok fitting. The test procedure was to store the samples for extended priods of time at 110°F, following which the specimens, the hydrazine and the evolved gas were inspected and analyzed.

Gas evolution data for the controls (apparatus containing hydrazine only) are shown by the solid lines in Figure 8. (The numbers refer to the runs of Reference 25). The curves are approximate, having been drawn by us through the points reported, but indicate average rates ranging from about .01 psi/day to 0.50 psi/day. This very large spread indicates that some random factor is present. In fact, gas evolution rates in the presence of most of the material specimens tested fell well within the range of the controls. The information reported is too comprehensive to be repeated here, but as an example four data points for 6Al-4V titanium are also shown in Figure 8 as the large circles.

The above experiments may be interpreted in the light of the discussions of hydrazine decomposition given above in Section IIC. First, it is a virtual certainty that gas evolution is taking place at specific active sites rather than uniformly over any one surface. Otherwise the spread in the data would not be observed. These reaction sites could come about either as a result of non-uniformity of the surfaces themselves, caused by contaminant substances which were not removed in the course of cleaning and passivation, or by generation of active sites during the cleaning process.

Again, the glass would be most likely to be affected by the above factors since it is inherently non-uniform and was cleaned with chromic acid and ammonium hydroxide. Traces of chromium ions, which could catalyze the decomposition, are difficult to remove and basic reagents tend to increase the number of hydroxyl groups on the glass surface. A larger number of hydroxyl groups will increase the number of sites where hydrazine may be absorbed. Metals, when treated with oxidizing cleaning and passivating reagents which are oxidizers, also generate metal ions but these ions are easier to remove than in the case of glass.

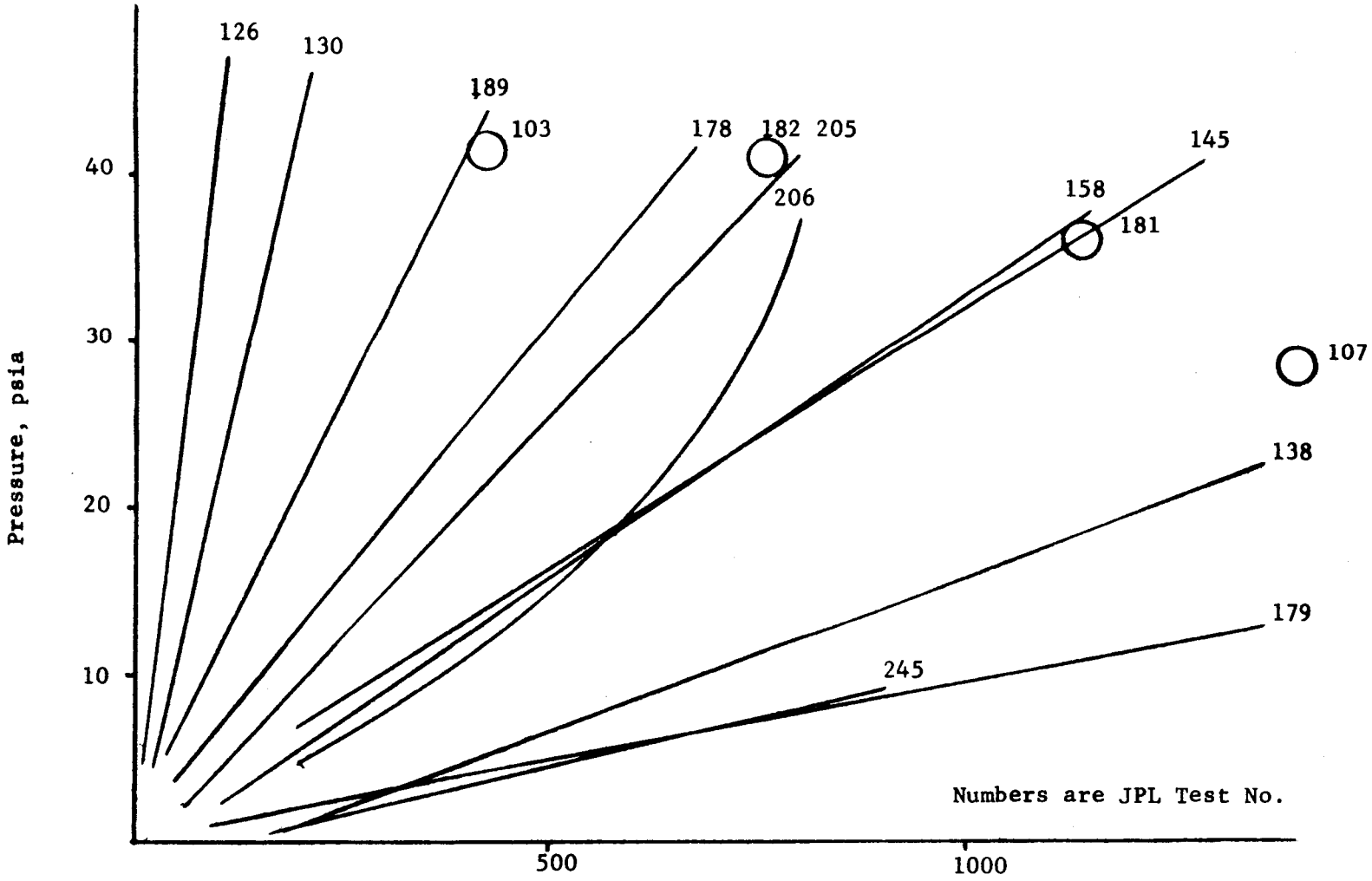


FIGURE 8

GAS EVOLUTION, JPL COMPATIBILITY TESTS

CONTROLS AND 6A1-4V TITANIUM SAMPLES

While catalytic reaction undoubtedly takes place on all surfaces exposed to vapor, and possibly those exposed to liquid, it is not known whether glass or metal is the principal contributor in the above experiments. However, unless non-reproducibility of the cleaning procedures would result in a 50 to 1 factor in reactivity, it would appear that reactive sites originally present in the glass surfaces might be the main source of gas evolution.

Stanford Research Institute, in their analysis of the subject data (Reference 26) has elected to consider only the controls represented by the three lowest curves of Figure 8. The circled points which represent 6Al-4V titanium (in combination with other materials), clearly gassed more than the three best controls, so SRI concludes 6Al-4V titanium is noncompatible. However, unless SRI has information not reported, it would appear that the stated conclusion might be unwarranted.

Additional data for 6Al-4V titanium in other propellant mixtures are shown in Table X. SRI concludes from these results that 6Al-4V titanium is compatible with the hydrazine-hydrazine nitrate mixture but noncompatible with the hydrazine - UDMH mixture. Again, it is difficult to understand the rationale since the specimens show gas evolution rates similar to the controls with no significant corrosion.

Fortunately, it is not necessary to resolve the finer points of the compatibility argument in order to determine acceptability of a material for use in a dual mode hydrazine system. The experimental evidence clearly shows that gas evolution, if it does occur, will be at a rate very much less than the planned electrolysis rate for a number of desirable materials of construction. Catalytic decomposition, so long as it is slower than the usage rate, would serve to relieve a small part of the burden on the electrolysis cell. It is not expected, however, that measurable catalytic decomposition will be observed.

Corrosion, if it takes place, is the only factor that could possibly be a problem. The measurements made by SRI on the JPL samples showed only very small weight changes for either titanium alloys or acid-treated 6061-T6 aluminum in either neat hydrazine or the mixtures. No results on the other materials are known to have been reported by SRI or JPL. Other investigators, however, generally report satisfactory performance for most stainless steels, aluminum alloys and titanium alloys. Also satisfactory are Teflon, Kel-F and many ethylene-propylene rubber compounds as well as polyethylene and polypropylene.

Our own experiments have been restricted to tests designed primarily to detect gross effects with the particular materials and combination of materials expected to be used in the developmental model cell. More elaborate tests were not undertaken because a program if the type conducted by JPL is beyond the scope of this contract and also because electrolyzing conditions could present new problems. The best evidence of compatibility will come from testing of the developmental model cell. We have had several laboratory cells in operation for periods up to several weeks in duration with no evidence of problems except for occasional staining of stainless steel and orange tinted discoloration of the hydrazine. Those effects are believed to have been caused by the presence of air in the apparatus.

TABLF X

JPL TESTS WITH 6AL-4V TITANIUM IN HYDRAZINE - HYDRAZINE NITRATE AND HYDRAZINE - UDMH (REFERENCE 25)

JPL Test No.	Storage Time years	Final Pressure, psia, 110°F	Weight Change %	Propellant
6A1-4V Titanium				
209	2.6	9.0	-0.0022	HZ-HN
210*	2.6	10.0	-0.0033	"
212	2.6	16.0	0.0000	"
213*	2.6	10.0	0.0000	"
Controls				
151	3.75	10.0		"
152	3.75	6.0		"
153	3.75	14.5		"
154	3.75	6.0		"
239	2.4	17.0		"
241	2.4	39.5		"
6A1-4V Titanium				
263	1.8	25.0	-0.0021	HZ-UDMH
264	1.8	7.5	-0.0021	"
265	1.8	11.5	-0.0021	"
266	1.8	15.5	-0.0032	"
267	1.8	10.0	-0.0032	"
268	1.8	15.0	-0.0032	"
269	1.8	13.0	-0.0021	"
271	1.8	23.0	-0.0042	"
272	1.8	8.0	-0.0022	"
273	1.8	16.5	-0.0074	"
274	1.8	8.5	-0.0055	"
Controls				
263A	1.8	12.5		
269A	1.8	33.5		

*Also 6061-T6 aluminum as part of sample tested

The actual compatibility tests were conducted in Pyrex glass tubes with a polyethylene seal. Various combinations of stainless steel, aluminum, titanium, graphite and glass cloth have been run, both at ambient temperature and +150°F, as shown in Table XI.

A few weeks after start of the tests, loss of liquid volume was noted in the +150°F samples, obviously because the polyethylene seal was inadequate. Several samples, especially those containing stainless steel, were discolored, probably because of air. In the ambient samples, some have discolored and others which had a better seal have not. Discoloration of hydrazine has also been observed in several of the laboratory cells after operation had been stopped for a day or more, whereas no discoloration had been detected during much longer periods of operation in which the generated gases continually purged the system.

The developmental model cell will be constructed of 6Al-4V titanium, aluminum, graphite, 99+% silica glass cloth, 304 stainless steel, Teflon and polypropylene. All of those materials are known to be compatible with neat hydrazine for at least a number of weeks at ambient temperature; they will be further evaluated under true system operating conditions during the course of Task V.

TABLE XI COMPATIBILITY TESTS

Experiment	Sample	Electrolyte	Material Sample	Wick Sample	Temperature		Results
					20°C (68°F)	70°C* (158°F)	
25	1	None	None	Glass Cloth		X	
	2	None	None	Glass Cloth	X		No change in 4 months
	3	2.79% oxalic acid	None	Glass Cloth		X	
	4	2.79% oxalic acid	None	Glass Cloth	X		No change in 4 months
	5	None	321 CRES	Glass Cloth		X	
	6	None	321 CRES	Glass Cloth	X		No change in 4 months
	7	2.79% oxalic acid	321 CRES	Glass Cloth		X	
	8	2.79% oxalic acid	321 CRES	Glass Cloth	X		Pale pink in 31 days (stopper loose.) No further change in 3 months.
43	1	None	None	Polyolefin Felt	X		Yellow color in N_2H_4.
	2	None	None	Dacron Felt	X		Yellow color in N_2H_4, in 3 min.; felt disintegrated in 15 minutes.
	3	None	None	Polyolefin Felt, after extraction with N_2H_4	X		No change in 2 1/2 months.
51	1	0.5% oxalic acid	Graphite +304 SS	None	X		No change in 1 month.
	2	0.5% oxalic acid	+6A1-4V Titanium	None	X		No change in 1 month.

* All samples stored at 158°F suffered failure of the polyethylene closure. In all cases the hydrazine has partially evaporated and discolored.

IX Zero Gravity Studies

A. Introduction

The dual mode hydrazine concept is adaptable to almost all spacecraft attitude control and maneuvering requirements, but the cold gas propulsion feature is of greatest interest for non-spinning, three-axis-stabilized vehicles. The system to be designed under this contract is for a specific large interplanetary vehicle according to the requirements described previously under Task I. During the cruise periods of the mission the gravitational forces will be very low, especially between attitude control pulses. In this section we shall consider the problem of managing the propellant ullage in order to supply gas-free liquid to the catalytic engines and liquid-free gas to the attitude control thrusters during the low-gravity phases of the mission.

Easiest of the two requirements is positive liquid expulsion from the propellant tank. A bladder or bellows would be difficult to mechanize in a tank containing an integral electrolysis cell, but screens which prevent passage of gas by surface tension effects should be adequate and may be accepted as state-of-the-art. Such screens have been demonstrated in models in which screens calculated to support a given liquid head against a given gravitational force showed good agreement between experiment and theory.

The liquid feed device may accordingly take the form of pie-pan shaped screens covering the outlet port, a close-fitting screen liner over part or all of the tank, a screen cannister located within the tank, or other similar configurations. Because of the flexibility of the devices and the relatively straightforward calculations needed to determine the proper screen size, no research in this area is likely to be needed under the present contract. Some calculations of required screen size are presented later in this section.

The gas-vent side is a more complex question, but is somewhat simpler for the dual mode system than for the most general case because the gas may be generated at a known location. Thus, it may be possible to trap a volume of gas sufficient for attitude control propulsion and allow only the remaining fraction to be released into the main ullage.

B. Mission Constraints

The mission profile provides two basic constraints for the gas vent design: the volume of gas needed for a given thrusting event; and the g-field limits.

With reference to the required gas volume, by JPL direction we are designing to a minimum impulse bit of 1.6×10^{-3} lb-sec. As a worst case, we may assume the configuration calls for four thrusters operating simultaneously in each of three axes at the minimum operating pressure. The minimum pressure, which will obtain immediately after the largest liquid engine thrust period, should be no less than about 90 psia to be compatible with catalytic engine operation. The temperature will be spacecraft ambient (70°F) if the tank is located within the main structure. The gas volume required is then:

$$V = \frac{1.6 \times 10^{-3}}{120 \text{ lb-sec/lb}} \times \frac{4 \times 3 \text{ lb-sec.}}{} \times \frac{454 \text{g}}{\text{lb}} \times \frac{3 \text{ mol}}{32 \text{ g}} \times \frac{82 \text{ ml atm}}{\text{Mol deg}}$$

$$\times \frac{294 \text{ deg}}{90/14.7 \text{ atm}} = 27 \text{ ml}$$

The minimum amount of hydrazine required for any of the system configurations is 22.6 lb, which occupies a volume of 10.3 liters. Thus, the worst case volume of trapped gas is considerably less than 1% of the smallest hydrazine tank. In actual system operation it is very unlikely that the worst case combination of curcumstances would occur. In a nominal case with smaller impulse bits, fewer thrusters operating simultaneously and higher system pressure, the volume of gas needed at any one time should be at least an order of magnitude smaller. There should be no practical difficulty in generating the needed amount of gas. In designing the development model of Task V, it will probably be desirable to fabricate a flexible unit capable of handling considerably larger gas volumes than needed to meet the very modest requirement of the present mission.

The gravitational forces experienced during the mission were estimated as follows:

1. Cruise Mode

From an estimate provided by JPL, the spacecraft may be 20 ft in diameter and have a moment of inertia of 14,000 slug ft^2. Then, if the propellant tank is located near the periphery and the total applied force (4 thrusters) is 0.16 lb,

$$\text{angular acceleration} = \frac{0.16 \times 10}{14 \times 10^3} = 1.14 \times 10^{-4} \text{ rad/sec}^2$$

$$\text{linear acceleration} = 1.14 \times 10^{-4} \times 10 = 1.14 \times 10^{-3} \text{ ft/sec}^2$$

$$= 3.55 \times 10^{-5} \text{ } g_o$$

For comparison, it may be noted that the angular accelerations during cruise mode maneuvering of the Ranger/Mariner class vehicles was of the order of 4.5×10^{-4} rad/sec^2, which for the above geometry would give a linear acceleration of 1.4×10^{-4} g.

For design purposes, a cruise mode field of 10^{-4} g_o is reasonable.

2. Midcourse

If the tank is aligned so that the retro force operates in a direction which tends to settle the liquid in the most favorable orientation, it is most likely from envelope considerations that the midcourse engine would operate along a

different axis. In most spacecraft this axis would probably be perpendicular to the retro axis, or lateral with respect to the cell. For a 20,000 lb spacecraft and a typical midcourse engine of 100 lbf thrust the acceleration would be

$$\frac{100}{20{,}000/32.2} = 5 \times 10^{-3}\ g_o$$

Design to lateral accelerations of the order of 10^{-2} to 10^{-1} g_o would appear to be reasonable.

3. Retro

While the retro thrust might be quite large, the cell and tank would be oriented in a direction which tends to settle the liquid away from the vent tube. Hence, there would be no low-g requirement to meet during retro.

C. Alternative Configurations

A number of possible configurations were examined. Originally it had been planned to use the "Christmas Tree" arrangement shown in Figure 9, which comprises a manifold of tubulatures terminating in non-wetting porous plugs. So long as any of the plugs were located within the ullage bubble, only gas would be vented. This device is similar to one developed by Bell Aerosystems under Air Force sponsorship. It was abandoned in the present case for two reasons. In the first place, this type device has not been tested in zero gravity and a possible failure mode may be envisioned if thermal gradients cause liquid to distill and condense on the inside surface of the porous plug. In such an event, when totally immersed in liquid, even a non-wetted plug may no longer bar passage of fluid. Secondly, the "Christmas Tree" design does not take advantage of the fact that in the dual mode system the gas bubble may be generated and trapped in a known location.

1. Straight Tube Configuration

The basic method selected for trapping the electrolysis gases is shown in Figure 10. The cell is composed of a cylindrical wick with screen wire electrodes on the inner and outer surfaces. The cell assembly is enclosed within an annular can with communication to the central cavity by a tube for gas passage and a wick which fits tightly enough to exclude gas but allows hydrazine to be drawn into the cell. The vent is a non-wetting Teflon-coated tube which protrudes into the hemispherical head end. Liquid is free to flow in and out through holes in the other end during pressure fluctuations.

Under zero gravity conditions, the ullage bubble will be stable in the hemispherical end (or adhere to the non-wetting vent tube if too small to fill the entire diameter). Since gas is injected into that area, it will not tend to migrate away. Any liquid which might be expelled from the electrolysis chamber will encounter a wetted wall and be drawn away from the vent.

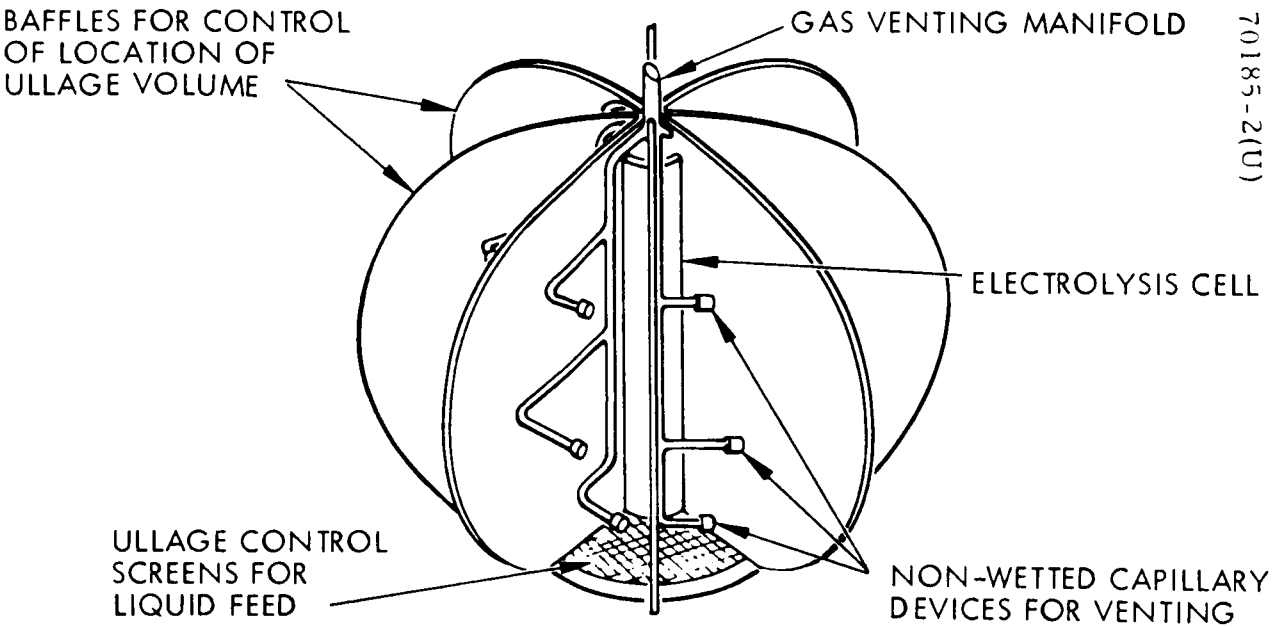
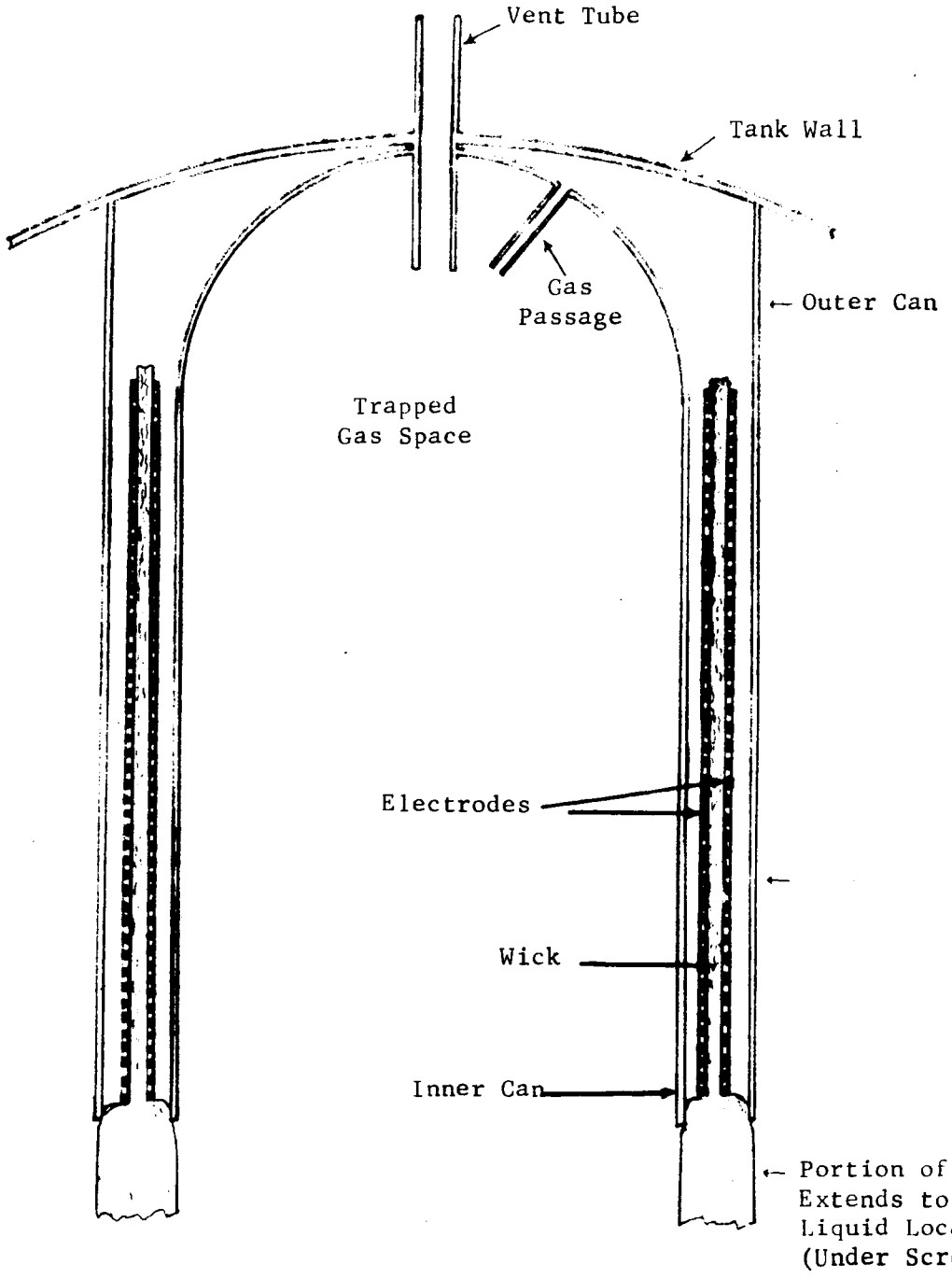
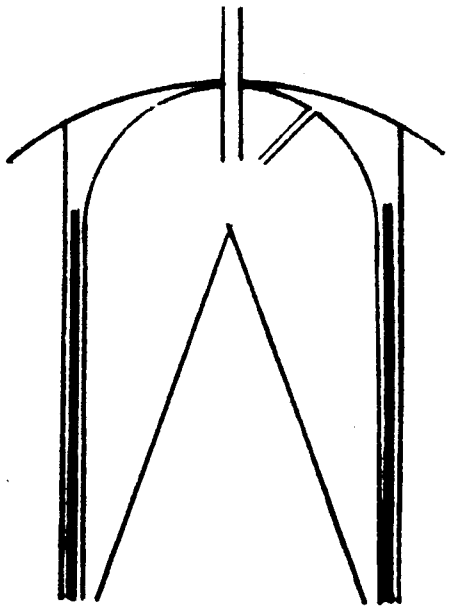


FIGURE 9

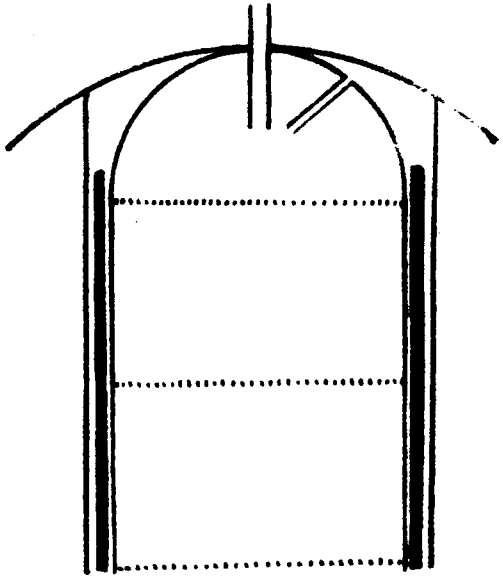
"CHRISTMAS TREE" CONFIGURATION



STRAIGHT TUBE CELL CONFIGURATION
FIGURE 10



CONE CONFIGURATION
FIGURE 11



SCREEN CONFIGURATION
FIGURE 12

The stability of this simple configuration is amendable to theoretical analysis. Two techniques were applied to evaluate the stability of the gas bubble in Figure 10.

The first approach was that of S. Boraas et al (27), who assumed that the critical gravity field, in which the bubble will no longer resist displacement along the longitudinal axis of the cell, may be taken to be that field wherein the buoyant forces exerted by the bubble are equal to the surface tension forces acting around the bubble perimeter. The mathematical treatment follows.

In zero and near-zero gravity, the stable configuration will be that for which the liquid-vapor interface is a section of a sphere, intersecting the wall at the contact angle. Thus, referring to Figure 13, $R = r/\cos \alpha$, and the total force due to surface tension, S, is:

$$S = \pi r^2 \left(\frac{2\sigma}{R}\right) \cos \alpha, \text{ where}$$

r = radius of cylinder

R = radius of curvature of the gas-liquid boundary

a = acceleration field

h = height of bubble under hydrostatic head

α = contact angle of liquid

V_b = portion of bubble volume under hydrostatic head

ρ = (density of liquid)-(density of gas)

And the volume of the bubble under the hydrostatic head is:

$$V_b = 1/3\pi h^2 \ (3R-h)$$

Substituting $h = r - R \cos (90 - \alpha)$, and $R = R/\cos \alpha$:

$$V_b = \frac{\pi r^3}{3 \cos^3 \alpha} (2 - 3 \sin \alpha \sin^3 \alpha)$$

If the bouyant force B is:

$$B = paV_b = \frac{pa\pi r^3}{3 \cos^3 \alpha} \ (2 - 3 \sin \alpha + \sin^3 \alpha),$$

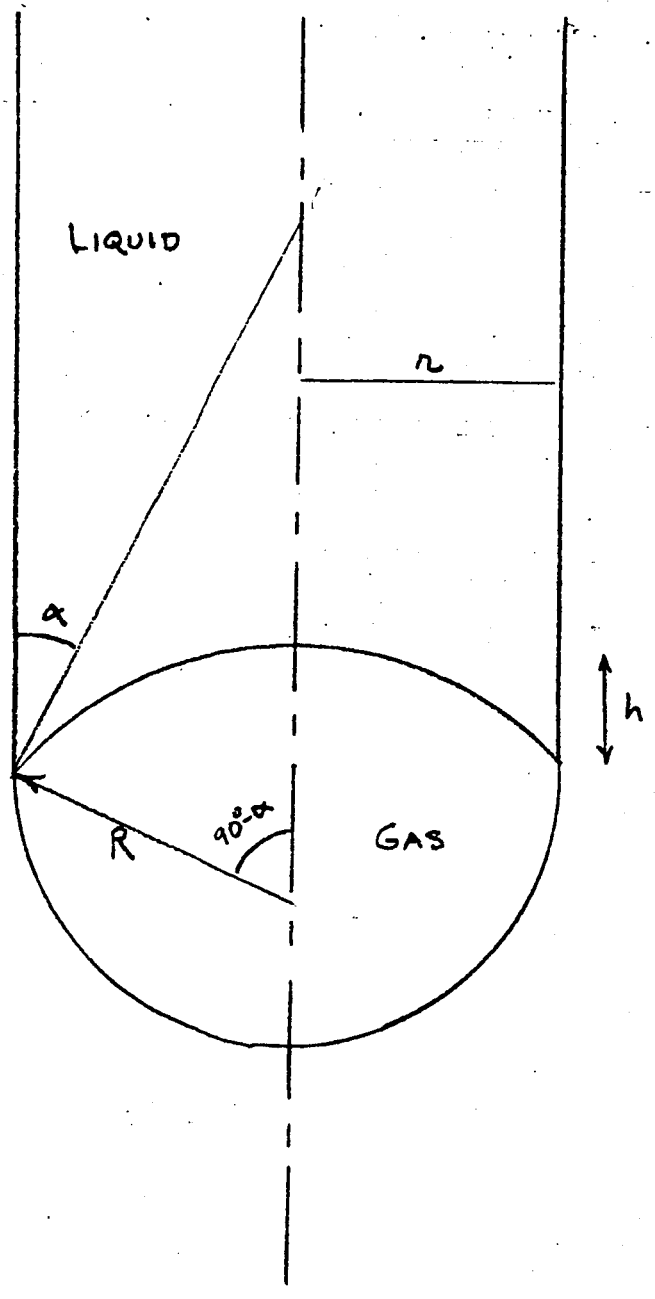


FIGURE 13

Geometry of Straight Tube Configuration

then, Equating S and B,

$$\frac{pa\pi r^3}{3\cos^3\alpha}(2 - 3\sin\alpha + \sin^3\alpha) = 2\pi r\sigma\cos^2\alpha,$$

$$\text{or } a = \frac{6\sigma}{r^2 p}\left[\frac{\cos^5\alpha}{2-3\sin\alpha+\sin^3\alpha}\right]$$

For the proposed cell design:

$\alpha \simeq 0$ for hydrazine in contact with metal surfaces

σ = 67 dynes/cm (hydrazine)

r = 2.5 cm (size of standpipe hole in the scrap Surveyor tank selected for Task V and of suitable size for the mission)

ρ = 1 g/cc

Therefore, a = 32.1 cm/sec^2, or, referred to standard gravity, 3.28 x $10^{-2} g_o$, which indicates that acceleration along the axis of the cell greater than 3.3 x 10^{-2} g_o will break the meniscus.

This analysis thus implies, with reference to the g-field estimates given previously, that there would be stability for cruise and turning maneuvers but a marginal condition at midcourse.

A more sophisticated analysis is that of Reynolds et al (28). Their treatment is based on the thermodynamic condition that the potential energy must be a minimum in an equilibrium state. They thus derived expressions for the stable configuration of an axisymmetric meniscus in terms of the strength of the g field; specifically, as a function of wetting angle and Bond Number.* Reynolds et al calculated the maximum bond number for which a liquid of given contact angle may support a stable meniscus in tubes having various wall shapes. For a liquid having 0^o contact angle in a straight walled tube, the critical Bond Number was found to be 0.85. Then,

* Bond number, defined as the ratio of gravitational to capillary forces, incorporates fluid density, acceleration, surface tension, and a characteristic length in a dimensionless term.

$$\frac{\rho a r^2}{\sigma} = \frac{1 \times a \times 2.5^2}{67} = .85$$

$$a = 9.12 \text{ cm/sec}^2, \text{ or } 9.3 \times 10^{-3} g.$$

This critical acceleration is about 1/3 of the value calculated by the method of Boraas et al, but would still predict stability during cruise mode and turning maneuvers. The reason for the difference between the two results has not been identified, but it may be noted that the constraint of Boraas et al to a spherical interface does not account for interface distortion prior to failure. It seems likely that the meniscus would be distorted at accelerations below the failure limit predicted by the Boraas treatment. Neither treatment predicts the details of what would happen when the meniscus became unstable under a g field.

It is of interest to repeat the above calculation in terms of what diameter tube would be effective in a -1g field:

$$r = \left(\frac{0.85\sigma}{\rho a}\right)^{1/2} = \left(\frac{0.85 \times 67}{1 \times 980}\right) = 0.241 \text{ cm}$$

In order to accommodate the 27 cm^3 of gas computed previously as a worst case requirement, this would require a six inch length straight tube. It would thus obviously be possible to build and test at -1 g a simple small diameter straight tube storage plenum which would satisfy the present requirements. There are possible difficulties with such a configuration, however, which will be discussed later.

2. Conical Configuration

A simple modification of the basic straight tube design is shown in Figure 11. It consists of a cone inserted into the gas storage space as shown. The acute angle found by the cone and wall of the cell could improve meniscus stability by virtue of the reduced meniscus diametral section and provide a positive force which would tend to displace any liquid present towards the base of the cone. This configuration was analyzed briefly. Reynolds et al (28) calculated the stability of flat annular menisci in parallel walled tubes by the thermodynamic method. They recommend that the non-parallel walls of the cone and cylinder may be approximated at a given point by a parallel-walled annulus of the same diamter, and suggested correction factors which could be applied to a liquid with contact angle other than 90°. The results for the present case are:

Outer Radius	Inner Radius	Critical Acceleration, g_o
2.5	2.0	0.085
2.5	1.5	0.026
2.5	0	0.009

It is concluded that the cone should improve stability by an order of magnitude for a nearly empty cavity but offers no improvement over the cylinder if the cavity is nearly full. It would be more satisfactory to employ a number of concentric slightly tapered baffles than a cone because performance would be essentially independent of the degree of filling and less volume would be wasted.

3. Screen Configuration

A possible problem with the straight tube design may arise if the electrolysis cell injects a liquid into the gas reservoir as might happen by distillation or excessive wicking of liquid into the cell. In a small diameter tube, liquid could accumulate until a slug was formed in the tube. Any sizable gas demand would almost surely result in expulsion of the liquid slug through the gas distribution system. A possible way to circumvent this difficulty is to use a large diameter tube incorporating one or more screens to stabilize the position of the bubble, as shown in Figure 12. If the screens are wetted, introduction of gas will expel liquid from the first compartment until it is completely empty. Then, gas will break through the wet screen and empty the other compartments in consecutive order. A calculation of screen size required to withstand various accelerations may be performed as follows:

$$D = \frac{2\sigma}{\Delta\rho\ \alpha\ gh}\ (\cos\theta + \sin\theta)$$

where

D = maximum pore size, cm

g = normal gravitational constant, 980 cm sec^{-2}

α = fraction of normal gravitational acceleration

σ = surface tension, 67 dynes/cm

$\Delta\rho$ = density difference (liquid-gas), 1 g/cm^2

θ = contact angle, 0^o

The anticipated maximum tank dimension is 36.5 cm, which is taken to be the hydrostatic head, h. The following table shows screen size required for several forces.

α, Fraction of Normal Earth Gravity	Screen Pore Diameter, cm
.001	3.84
.01	3.84×10^{-1}
.1	3.84×10^{-2}
1.0	3.84×10^{-3}
10.0	3.84×10^{-4}

It is seen that the estimated gravitational forces may be managed by a very coase screen of the order of 1 cm in diameter. Even more of interest is that a 35 micron screen should withstand normal gravity. Not only could a very large safety factor be obtained by a readily available screen but it should also be possible to build a device which could be tested in normal Earth gravity. This advantage is not realized in the other configurations; even without analysis it is seen that the other configurations would not be stable in an inverted position.

The screen configuration is preferred because it can be tested in all positions in the laboratory. It is reasonable to suppose that any device which is demonstrated to be satisfactory in adverse normal gravity will perform properly in low gravity.

D. Analytical Conclusions

The compartmented screen design of Figure 12 has much greater potential stability than the other configurations considered. The analysis of the simple straight tube cavity was of interest, however, because it indicated that success is probable even in the event of a screen failure.

It is desirable to build the screen device, which has capacity considerably in excess of the present mission requirements, if it can be done without significant weight penalty. Such a device not only can be tested in -1 g, but also would be suitable for a broad range of applications, without redesign.

E. Zero-g Laboratory Device

As mentioned, a possible problem with the selected design is conceivable if the electrolysis cell should inject liquid along with gas. Although at equilibrium the liquid would be positioned behind the separator screen, it is possible that a slug of liquid would accumulate and only be slowly removed from the gas reservoir. One way to avoid this problem would be to line the entire chamber with fine screen until is expelled.

A one compartment model was constructed from 2 inch diameter Plexiglass tube as shown in Figure (14A). In the actual device several such compartments may appear in series. Ten micron pore size screen forms the divider and also lines the cavity, as shown in (B). The cavity is filled initially with liquid (C), which is expelled upward through the divider screen by gas from vessel (D). Pressure of the entering gas is controlled by the liquid head (E).

Figure 14 shows the cavity at an intermediate point in the expulsion where the ullage bubble has occupied the full available diameter. Pumping gas into the cavity will cause liquid to move up the screen in the manner shown in the inset.

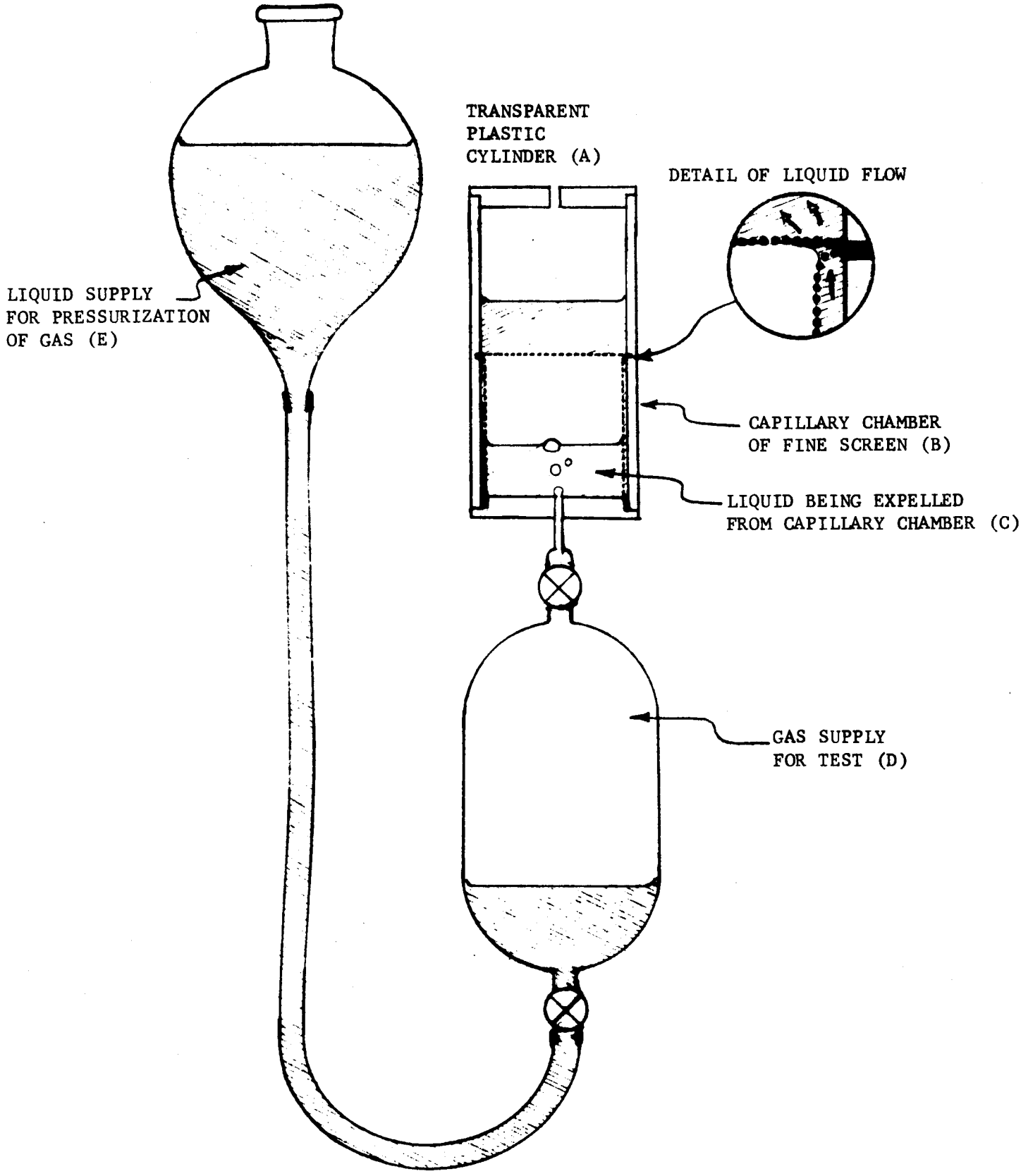


FIGURE 14

APPARATUS FOR DEMONSTRATION OF EXPULSION OF LIQUID
FROM GAS STORAGE CHAMBER UTILIZING CAPILLARY FORCES

If gas is introduced too rapidly, the capillary flow of liquid will not be able to keep up with demand and bubbles will break through the divider screen. This behavior has been observed in experiment. Gas may displace all of the liquid in several minutes of time, but not in seconds. Decreasing the screen pore size would be expected to reduce necessary expulsion time.

The missions of present interest probably would require expulsion times in the order of hours rather than seconds so that the ten micron screen should be adequate. Note that screens are inherently non-uniform in pore size and the absolute micron rating of a given specimen must be determined by bubble breakthrough test. Ten microns should be quite conservative, however, as previous calculations had indicated about 35 micron screen should support the highest liquid head anticipated.

The action of the screen in effecting gas-liquid separation may be elucidated by the following mathematical treatment.

Consider the device shown in Figure 15, which is a long tube containing a coaxial screen. The screen is formed into a closed cavity, either by another piece of screen or by a solid closure as shown, and contains the ullage bubble. With acceleration in the indicated direction the settling force will tend to displace liquid in the downward direction.

If gas is injected into the ullage cavity, the pressure rises and liquid flows through the screen into the annulus. This process continues until the hydrostatic head, h, experts a force equal to the pressure difference across the screen at the level of point A. Gas may be admitted until the differential pressure force exceeds surface tension forces. At that time the bubble will break through the largest pore in the screen. The total hydrostatic head which may be supported by a given screen may be calculated by equating the forces P_L and P_G or, $\Delta\rho ah = \frac{2\sigma}{d}$.

where

$\Delta\rho$ = density difference between gas and liquid

a = acceleration

h = liquid hydrostatic head

σ = surface tension of liquid

d = effective pore diameter of the screen.

With hydrazine in a field of -1 g and a 10 micron screen,

$$h = \frac{2\sigma}{\Delta\rho ad} = \frac{2 \times 67}{1 \times 980} \times 10^{-3} = 137 \text{ cm}$$

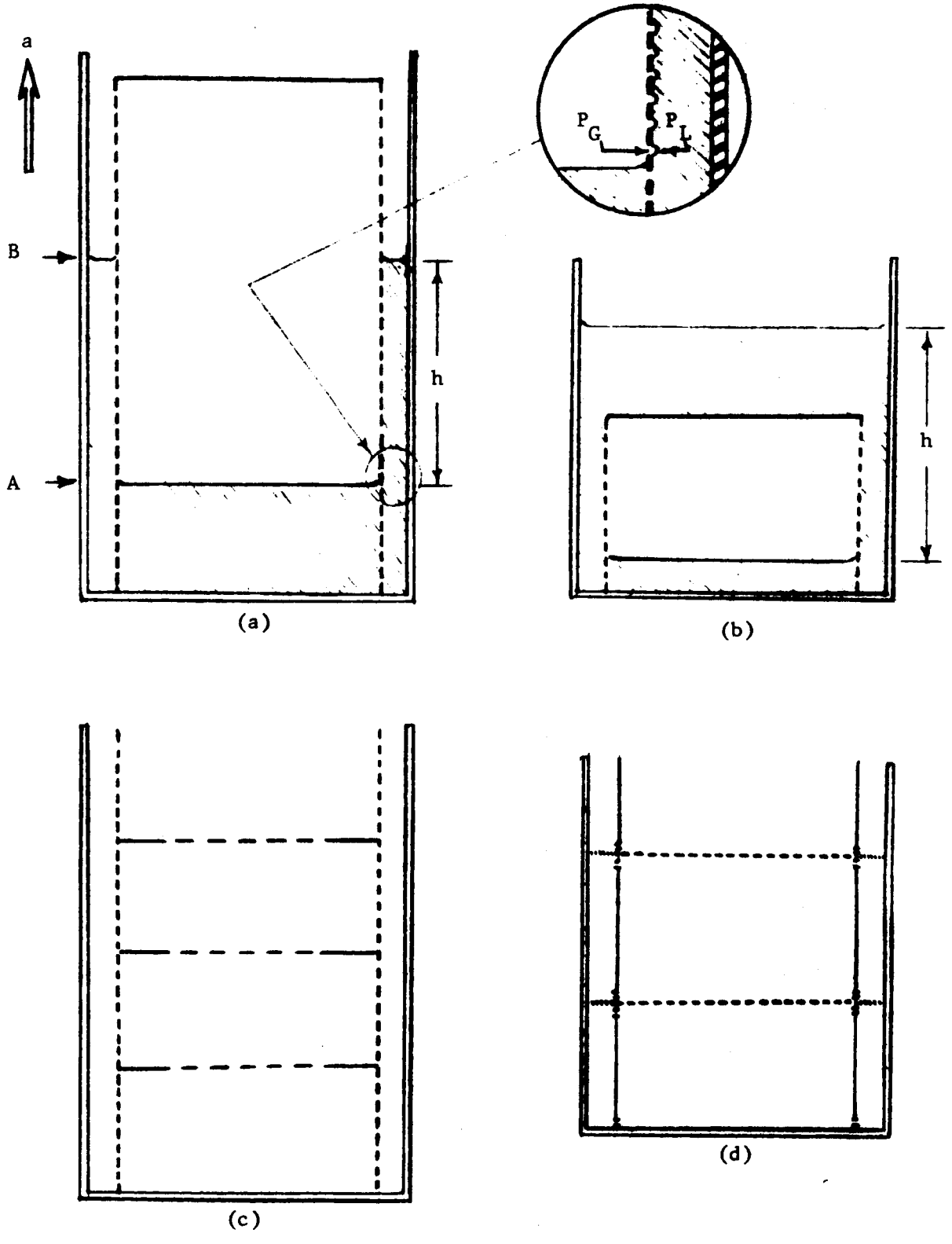


FIGURE 15
VARIOUS SCREEN CONFIGURATIONS

or, a head approximately four times larger than the maximum anticipated tank dimension may be supported.

Note that the screen cavity also could be shorter than the liquid head as shown in Figure 15b. The effective hydrostatic head is now as indicated and the analysis is identical with that above.

If a series of compartments as shown in Figure 15c is employed and gas introduced into C, the compartments will be drained in the order CDEF. In this case, however, some provision must be made to ensure bubble breakthrough into the next compartment rather than into the annulus where gas could exit from the system directly. This may be accomplished, as shown, by a larger pore screen in the dividers or, alternatively, by finer pore screen dividers between the screen and chamber wall. In the latter case, the screen cylinder may be replaced by a wall with a small opening into each compartment as shown in Figure 15d.

The above designs are based on the fact that, under sufficient differential pressure, the bubble will always break through the largest available opening but liquid may flow through a very fine screen with only a minute pressure drop, providing the liquid is in communication with another body of liquid on the other side of the screen. It is true that liquid flow through a fine screen is slow with low differential pressure but gas generation rate is also very slow and no problem is anticipated.

It may be noted that the above calculations apply equally well to the problem of liquid expulsion from a tank, for the same capillary forces are in effect. Thus, the same size screen is required to prevent entry of gas into the liquid compartment as was found necessary to contain the gas bubble in its storage compartments.

X Conclusions Relative to Task V

The experimental and analytical work permit the following conclusion relative to the forthcoming Task V effort.

A. A graphite or carbon anode, in conjunction with a 304 stainless steel or aluminum anode, will give suitable electrolysis rates, at any desired applied potential up to 28 volts, without significant erosion or chemical attack.

B. Hydrazinium oxalate, in small amounts (< 1%) will impart adequate conductivity to propellant-grade hydrazine, and will quantitatively provide hydrogen and nitrogen gases as electrolysis products. The latter gases are not significantly soluble in hydrazine.

C. There is no cause for concern regarding the controllability of the electrolysis process under possible mission conditions.

D. Glass cloth is a suitable wicking material for low gravity conditions.

E. Suitable materials of for the Task V effort which are compatible with hydrazine include 6A1-4V titanium, aluminum, graphite, 00+% silica glass cloth, 304 stainless steel, Teflon and polypropylene.

F. A zero-g gas venting device is feasible which can be tested at -1 g and would have every likelihood of operating successfully under mission conditions. The liquid expulsion side of the dual mode hydrazine system can be handled adequately by screen devices which have already been demonstrated in other programs and need not be studied under the resent effort.

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ERRATA TO SUMMARY REPORT, TASK IV

P. 51 last paragraph

. . . minimum impulse bit of 1.6×10^{-3} lb-sec.

P. 52

$$V = \frac{1.6 \times 10^{-3} \times 4 \times 3 \text{ lb-sec.}}{120 \text{ lb-sec/lb}} \times \frac{454 \text{ g}}{\text{lb}} \times \frac{3 \text{ mol}}{32 \text{ g}} \times$$

$$\frac{82 \text{ ml atm}}{\text{Mol deg}} \times \frac{294 \text{ deg}}{90/14.7 \text{ atm}} = 27 \text{ ml}$$

P. 59 Paragraph 3

27 cm^3

P. 63 Paragraph 5

$$\Delta p_{ah} = \frac{2\sigma}{d}$$