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SPACECRAFT NITROGEN GENERATION

FINAL REPORT

by

R.D. Marshall, J.N. Carlson,
J.D. Powell and K.K. Kacholia

December, 1974

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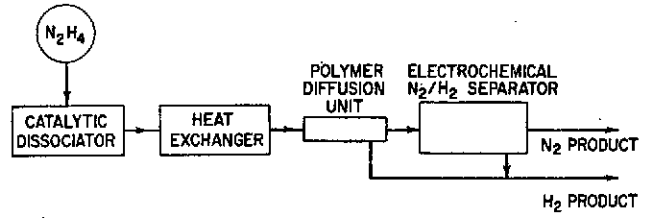
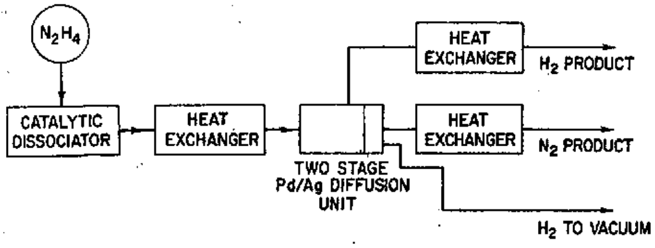
SYSTEMS EVALUATED

POLYMER-ELECTROCHEMICAL N_2 GENERATION SYSTEM



PALLADIUM/SILVER N_2 GENERATION SYSTEM



Prepared Under Contract No. NAS 2 - 7057

by

Life Systems, Inc.
Cleveland, Ohio 44122

for

AMES RESEARCH CENTER

National Aeronautics & Space Administration

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FOREWORD

The development work described herein was conducted by Life Systems, Inc. during the period May 1, 1973 to January 1, 1975 under NASA Contract NAS2-7057. The Program Manager was Richard D. Marshall. Technical support was provided as follows:

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SUMMARY

A program was successfully completed to evaluate two spacecraft Nitrogen (N_2) Generation Systems based on the catalytic dissociation of hydrazine (N_2H_4). In the first system, liquid N_2H_4 is catalytically dissociated to yield an N_2 and hydrogen (H_2) gas mixture. Separation of the N_2/H_2 gas mixture to yield N_2 and a supply of H_2 is accomplished using a Polymer-Electrochemical N_2/H_2 Separator. In the second system, the N_2/H_2 gas mixture is separated in a two-stage Palladium/Silver (Pd/Ag) N_2/H_2 Separator. The program culminated in the successful design, fabrication, and testing of a N_2H_4 Catalytic Dissociator, a Polymer-Electrochemical N_2/H_2 Separator, and a two-stage Pd/Ag N_2/H_2 Separator. The hardware developed was sized for an N_2 delivery rate of 6.81 kg/d (15 lb/day). Experimental results demonstrated that both spacecraft N_2 generation systems are capable of producing 6.81 kg/d (15 lb/day) of 99.9% pure N_2 at a pressure greater than or equal to 1035 kN/m^2 (150 psia).

The Polymer-Electrochemical N_2/H_2 Separator developed successfully integrated a Polymer Diffusion Unit and an Electrochemical N_2/H_2 Separator. Control and monitor instrumentation was developed and provided for fully automatic integrated operation. Ground Support Accessories (GSA) were developed to simulate fluid and electrical interfaces during testing. The test program completed consisted of Polymer Diffusion Unit and Electrochemical N_2/H_2 Separator checkout testing, a Shakedown Test, and a 200-hour Design Verification Test (DVT). Test results obtained at the design point demonstrated the Polymer-Electrochemical N_2/H_2 Separator to be an effective means of performing the N_2/H_2 separation process. During the DVT, the Polymer-Electrochemical N_2/H_2 Separator developed delivered 6.81 kg/d (15 lb/day) of 99.6% to 99.9% (by volume) pure N_2 at 1035 kN/m^2 (150 psia) and 0.98 kg/d (2.14 lb/day) of 97.5% to 98.7% (by volume) pure H_2 at 172 kN/m^2 (25 psia). The Electrochemical N_2/H_2 Separator module required only 25 watts of power. The polymer membrane material used in the present Polymer Diffusion Unit design, however, is not compatible with ammonia (NH_3) concentrations above 0.5%. Direct integration with the N_2H_4 Catalytic Dissociator is not possible until a compatible membrane is developed or the 2.5% NH_3 concentration in the N_2H_4 Catalytic Dissociator product stream is reduced to the safe level.

The two-stage Pd/Ag N_2/H_2 Separator developed consisted of two series-connected Pd/Ag Diffusion Units. Each unit represented a stage in the separation process. Approximately 85% of the H_2 in the feed gas was removed in the first stage and recovered at a useable pressure of 172 kN/m^2 (25 psia). The remaining H_2 was removed in the second stage to vacuum. Ground Support Accessories were developed to test the two-stage Pd/Ag N_2/H_2 Separator. Testing consisted of checkout testing, a Shakedown Test, and a 200-hour DVT. Test results obtained at the design point demonstrated the two-stage Pd/Ag N_2/H_2 Separator to be a simple and effective means of performing the N_2/H_2 separation process. During the DVT, the two-stage Pd/Ag N_2/H_2 Separator developed delivered 6.81 kg/d (15 lb/day) of 99.1% to 99.9% (by volume) pure N_2 at 1691 kN/m^2 (245 psia) and 0.83 kg/d (1.82 lb/day) of ultrapure (greater than 99.9999% by volume) H_2 at 172 kN/m^2 (25 psia). In addition, the Pd/Ag N_2/H_2 Separator is compatible with NH_3 and can be directly integrated with the N_2H_4 Catalytic Dissociator.

The N_2H_4 Catalytic Dissociator developed was used successfully to dissociate 7.78 kg/d (17.14 lb/day) of liquid N_2H_4 (5.4 cm^3/min) and deliver a N_2/H_2 gas mixture for subsequent separation. Instrumentation was developed to control N_2/H_2 Catalytic Dissociator operation and monitor performance. Ground Support Accessories were developed to simulate fluid interfaces during testing. Testing consisted of checkout testing, a Shakedown Test, parametric tests to determine the effect of temperature, pressure and N_2H_4 flow rate, and a 100-hour DVT. Based on the test results, modifications to the N_2H_4 Catalytic Dissociator design were recommended to lower the NH_3 concentration in the product gas stream from 2.5% to 0.5% (by volume).

To support the testing of the hardware developed, cost-effective procedures were defined and evaluated to analyze the product gas streams for N_2, H_2, NH_3, and N_2H_4 concentrations. Based on the literature and product survey completed, gas chromatography was selected and gas chromatographic analysis procedures were established.

INTRODUCTION

Future long-term manned spacecraft missions will utilize an atmosphere of nitrogen (N_2) and oxygen (O_2). Space vehicle gas leakage and cabin depressurization requirements necessitate on-board storage of the primary cabin atmospheric constituents N_2 and O_2. The N_2 component of air can be stored as liquid hydrazine (N_2H_4) and the N_2H_4 catalytically dissociated to yield a mixture of N_2 and hydrogen (H_2). The N_2/H_2 mixture is then separated to yield the makeup N_2. The excess supply of H_2 would be available for use in the reduction of metabolic carbon dioxide (CO_2).

Two attractive spacecraft N_2 Generation Systems have been identified based on the catalytic dissociation of hydrazine (N_2H_4)(1,2). The two systems are presented schematically in Figures 1 and 2. The first system (Figure 1) uses a Polymer Diffusion Unit to separate 80 to 85% of the H_2 from the N_2 product stream. The remaining H_2 is then removed in an Electrochemical N_2/H_2 Separator. The second system (Figure 2) uses a two-stage Palladium/Silver (Pd/Ag) N_2/H_2 Separator. The first stage separates 80 to 85% of the H_2 from the N_2 product stream and the second stage removes the remaining H_2 to space vacuum.

The objective of the present program was to evaluate the two N_2 Generation Systems by developing the Polymer-Electrochemical N_2/H_2 Separator, the two-stage Pd/Ag N_2/H_2 Separator, and the N_2H_4 Catalytic Dissociator. The program was based on a nominal N_2 generation rate of 6.81 kg/d (15 lb/day) with a possible range in N_2 generation rates of 3.18-6.81 kg/d (7-15 lb/day). The H_2 byproduct delivery rate associated with the N_2 generation rates is 0.45-0.98 kg/d (1.0-2.14 lb/day).

The program was divided into three phases:

1. Development of the Polymer-Electrochemical N_2/H_2 Separator.

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(1) All references cited are listed at the end of this report.

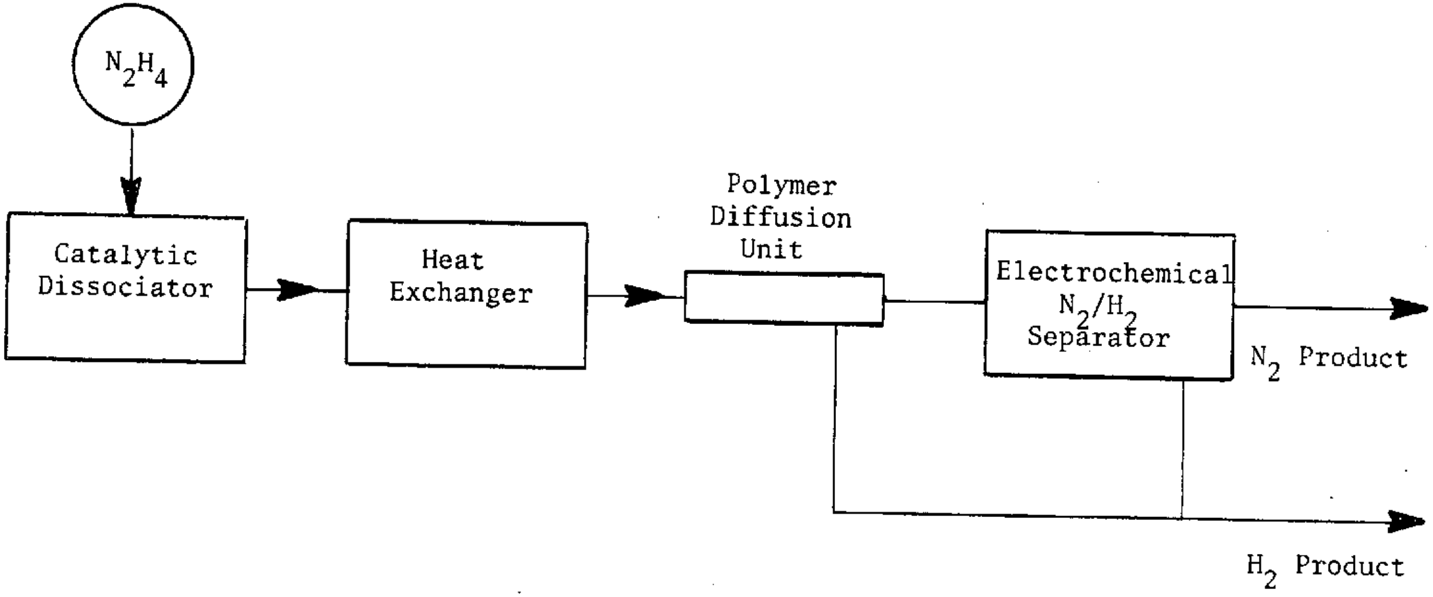

FIGURE 1 POLYMER-ELECTROCHEMICAL N_2 GENERATOR SYSTEM BLOCK DIAGRAM

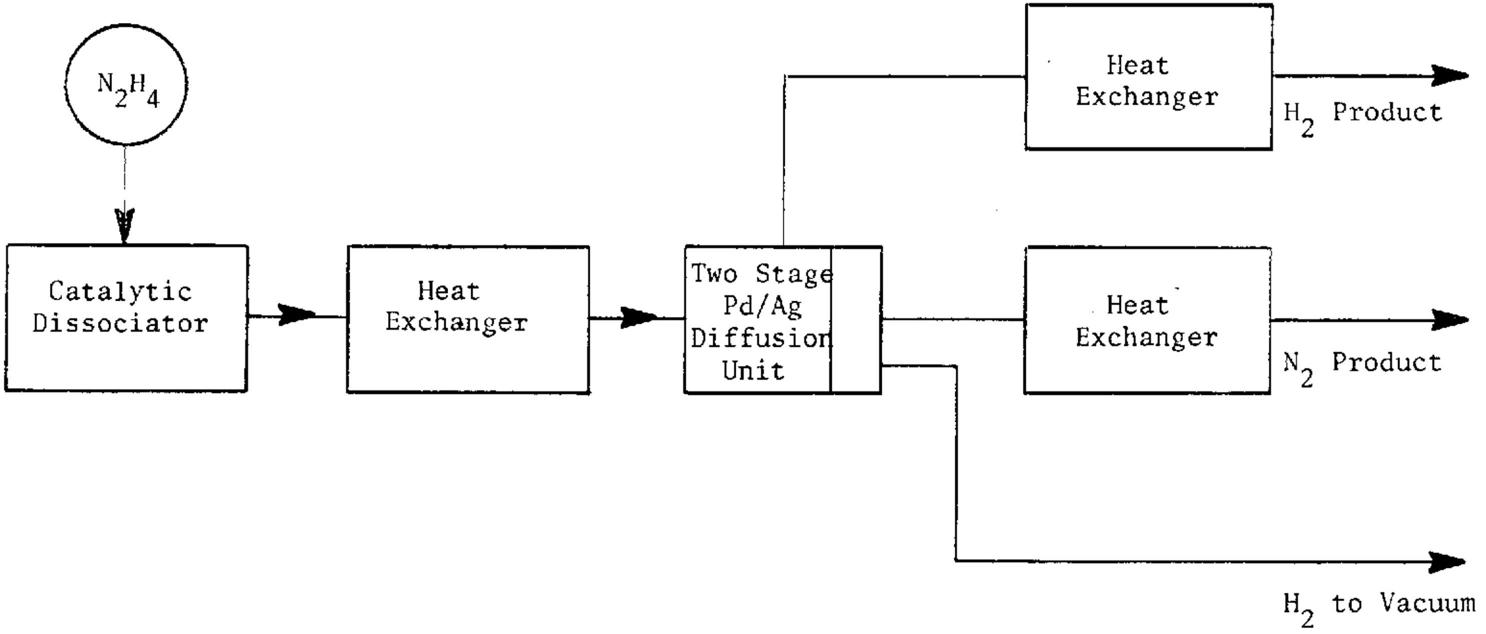

FIGURE 2 PALLADIUM/SILVER N_2 GENERATOR SYSTEM BLOCK DIAGRAM

2. Development of the two-stage Pd/Ag N_2/H_2 Separator.

3. Development of the N_2H_4 Catalytic Dissociator.

In parallel to the development phases, a literature and product survey was completed to identify and evaluate methods and procedures to analyze the process gas streams for N_2, H_2, NH_3, and N_2H_4 concentrations.

To accomplish the above, the program was divided into six tasks and program management functions. The specific objectives of the six tasks were to:

1. Design and develop a Polymer-Electrochemical N_2/H_2 Separator to deliver 6.81 kg/d (15 lb/day) of N_2 from an N_2/H_2 gas mixture based on the dissociation of N_2H_4.

2. Design and develop GSA to test the Polymer-Electrochemical N_2/H_2 Separator.

3. Conduct a test program on the Polymer-Electrochemical N_2/H_2 Separator, including component checkout testing, a Shakedown Test, and a 200-hour Design Verification Test (DVT).

4. Design and develop a two-stage Pd/Ag N_2/H_2 Separator to deliver 6.81 kg/d (15 lb/day) of N_2 from a N_2/H_2 gas mixture based on the dissociation of N_2H_4, including the development of the GSA required to test the Pd/Ag N_2/H_2 Separator, and conduct a test program on the N_2/H_2 Separator, including component checkout tests, a Shakedown Test, and a 200-hour DVT.

5. Design and develop a N_2H_4 Catalytic Dissociator to dissociate 7.78 kg/d (17.14 lb/day) of N_2H_4, including the development of the GSA required to test the N_2H_4 Catalytic Dissociator, and conduct a test program on the N_2H_4 Catalytic Dissociator, including component checkout tests, a Shakedown Test, parametric tests (temperature, pressure, and flow rate), and a 100-hour DVT.

6. Evaluate and establish cost-effective procedures to analyze the process gas streams associated with a spacecraft N_2 Generation System based on the catalytic dissociation of N_2H_4.

The objectives of the program were met. The following sections summarize the work completed and are organized according to the six program tasks.

POLYMER-ELECTROCHEMICAL N_2/H_2 SEPARATOR

The function of the Polymer-Electrochemical N_2/H_2 Separator is to separate 6.81 kg/d (15 lb/day) of N_2 from 0.98 kg/d (2.14 lb/day) of H_2 and to deliver the N_2 product gas at an elevated pressure for spacecraft N_2 resupply applications. The system consists of a Polymer Diffusion Unit and an Electrochemical N_2/H_2

Separator module, which actually perform the N_2/H_2 separation process, and the mechanical and electrical components which enable automatic system operation. The system is protected by monitoring instrumentation to shut the system down should a critical parameter exceed the tolerance level.

System Design

Table 1 presents the design specifications for the Polymer-Electrochemical N_2/H_2 Separator. The design specifications were established based on envisioned performance characteristics for the two N_2/H_2 separator designs.

Design Considerations

The primary design goal was to integrate a Polymer Diffusion Unit and an Electrochemical N_2/H_2 Separator including the controls and instrumentation required for automatic system operation. A readily available, "off-the-shelf" Polymer Diffusion Unit was selected to minimize development time and costs. The polymer unit used, however, does not represent an optimum design. Further, the polymer membrane used in the unit is not compatible with ammonia (NH_3). Direct integration with a N_2H_4 Catalytic Dissociator, therefore, is not possible. A new membrane that has improved N_2/H_2 separation characteristics and is compatible with NH_3 is currently under development, but was not available at the time the present program was conducted(3). All other components including the Electrochemical N_2/H_2 Separator were developed toward the end-item application, i.e., direct integration with the N_2H_4 Catalytic Dissociator. A modular packaging concept was selected so that the present Polymer Diffusion Unit could be replaced at a later date. Components other than the Polymer Diffusion Unit were packaged together and connected to the polymer unit. The objective was not to detain the system hardware development because a suitable polymer unit was not available.

Polymer N_2/H_2 Separator Design

Figure 3 is a functional schematic of the polymer diffusion unit. Hollow polyester fibers are formed into a tube bundle resembling a shell and tube heat exchanger. The tube bundle is fastened to the manifold plates at each end of the unit using an epoxy resin. The N_2/H_2 mixture is manifolded through the inside of the polyester fibers at an elevated pressure. Hydrogen and a small quantity of N_2 then diffuse through the fibers and are collected on the shell side at a lower pressure. The H_2-depleted N_2/H_2 stream exhausts the unit for further separation in the Electrochemical N_2/H_2 Separator. The use of hollow fiber technology allows the large membrane surface area required for the separation, approximately 93 m^2 (1000 ft^2), to be packaged in a small volume.

Electrochemical N_2/H_2 Separator Design

A functional schematic of an electrochemical N_2/H_2 Separator cell is presented in Figure 4. The electrochemical cell consists of two porous electrodes separated by an aqueous potassium hydroxide (KOH) electrolyte solution. Electrolyte is retained between the electrodes in a thin asbestos matrix. Compartments adjacent to the electrodes provide passageways for distributing the N_2/H_2 mixture and for collecting the separated H_2.

TABLE 1 POLYMER-ELECTROCHEMICAL N_2/H_2 SEPARATOR DESIGN SPECIFICATIONS

N_2/H_2 Feed	
Source	Premixed N_2/H_2
Flow Rate	
Nominal, kg/d (Lb/Day)	7.78 (17.14)
dm^3/min (Slpm)	12.2 (12.2)
Minimum, kg/d (Lb/Day)	3.6 (8.0)
dm^3/min (Slpm)	5.7 (5.7)
Maximum, kg/d (Lb/Day)	8.2 (18.0)
dm^3/min (Slpm)	12.8 (12.8)
Composition (by volume)	
N_2, %	33
H_2, %	67
Temperature, K(F)	293 - 298 (68 - 77)
Pressure	
Nominal, kN/m^2 (Psia)	1242 (180)
Minimum, kN/m^2 (Psia)	1104 (160)
Maximum, kN/m^2 (Psia)	2070 (300)
N_2 Product	
Flow Rate	
Nominal, kg/d (Lb/Day)	6.8 (15.0)
dm^3/min (Slpm)	4.0 (4.0)
Minimum, kg/d (Lb/Day)	3.2 (7.0)
dm^3/min (Slpm)	1.9 (1.9)
Maximum, kg/d (Lb/Day)	6.8 (15.0)
dm^3/min (Slpm)	4.0 (4.0)
Purity (by volume)	
Minimum, %	99.0
Maximum, %	99.9+
Temperature, K(F)	293 - 298 (68 - 77)
Pressure	
Nominal, kN/m^2 (Psia)	1035 (150)
Minimum, kN/m^2 (Psia)	621 (90)
Maximum, kN/m^2 (Psia)	1035 (150)

-continued-

Table 1 - continued

H_2 Product	
Flow Rate	
Nominal, kg/d (Lb/Day)	0.98 (2.14)
dm^3/min (Slpm)	8.2 (8.2)
Minimum, kg/d (Lb/Day)	0.45 (1.0)
dm^3/min (Slpm)	3.8 (3.8)
Maximum, kg/d Lb/Day)	0.98 (2.14)
dm^3/min (Slpm)	8.2 (8.2)
Purity (by volume)	
Minimum, %	95.0
Maximum, %	99.0+
Temperature, K(F)	293 - 298 (68 - 77)
Pressure	
Nominal, kN/m^2 (Psia)	172 (25)
Minimum, kN/m^2 (Psia)	104 (15)
Maximum, kN/m^2 (Psia)	310 (45)
Electrical Power	
Supply Voltage, VDC	28±4
Supply Voltage, VAC	115±10
Hz	60 or 400
Purge Supply	
Type Gas	N_2
Pressure, kN/m^2 (Psia)	310 (45)
Water Supply	
Pressure, kN/m^2 (psia)	310 (45)
Coolant Supply	
Type	Water
Temperature, K(F)	277 - 280 (40 - 45)

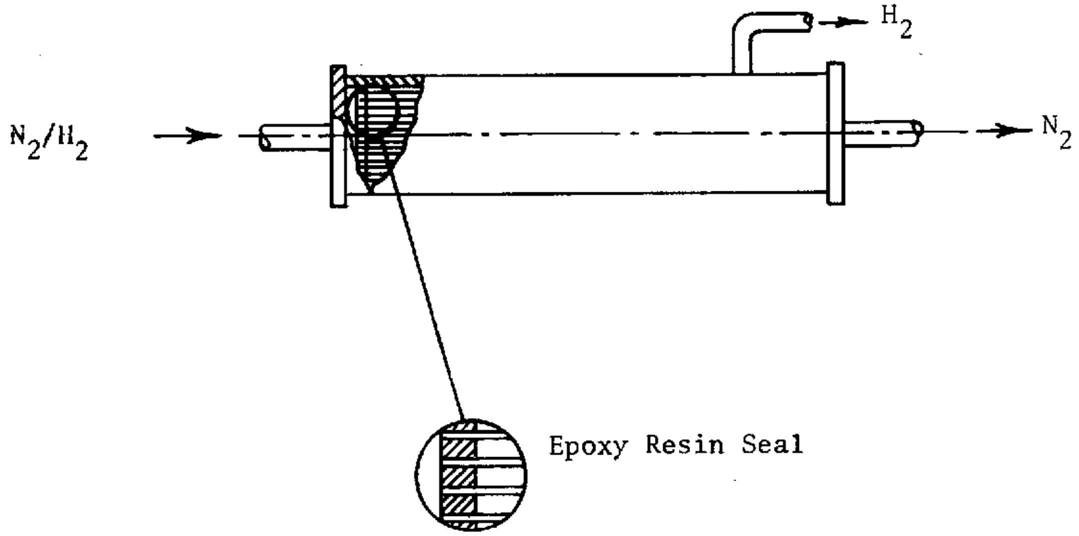

FIGURE 3 POLYMER DIFFUSION UNIT FUNCTIONAL SCHEMATIC

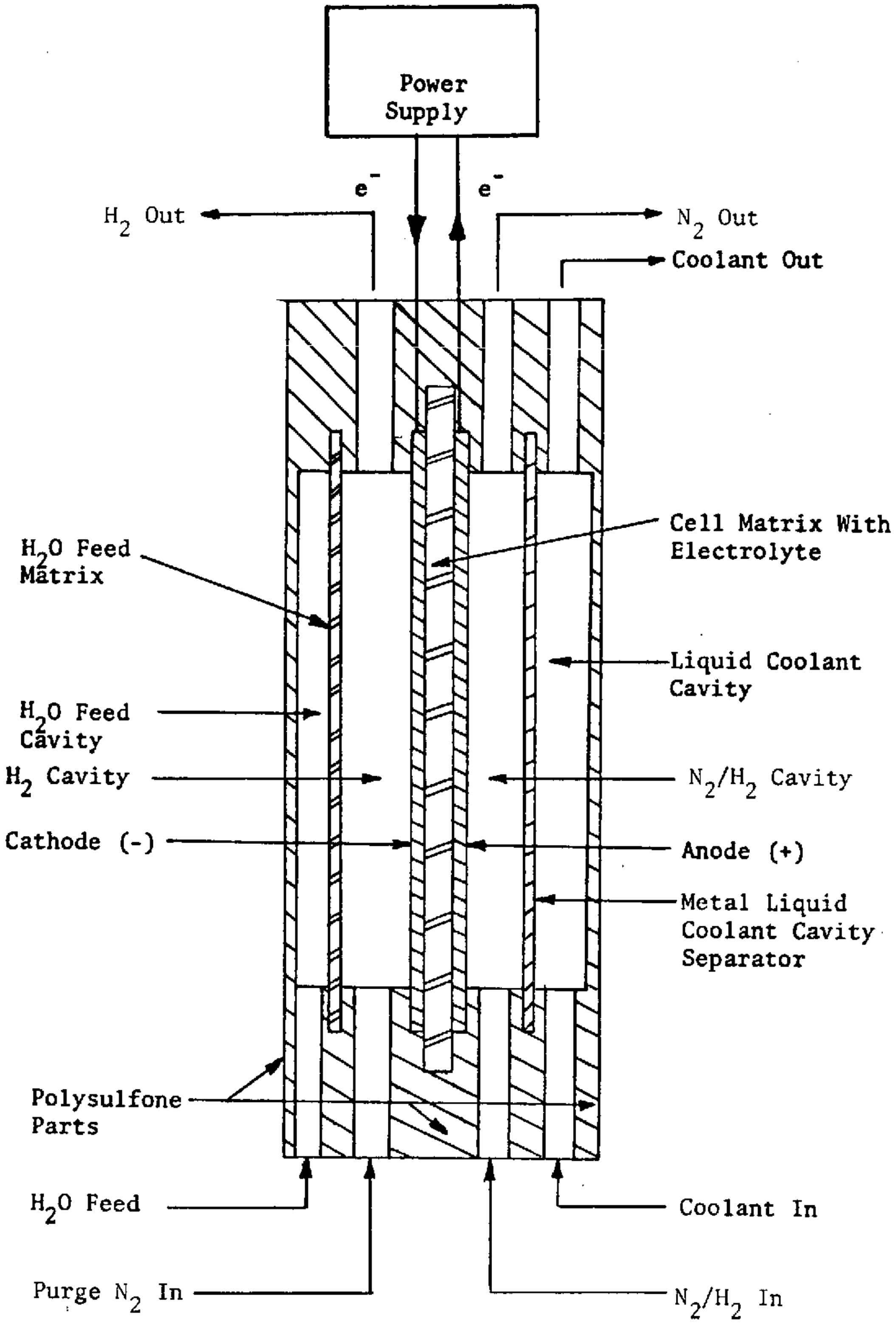

FIGURE 4 ELECTROCHEMICAL N_2/H_2 SEPARATOR MODULE FUNCTIONAL CELL SCHEMATIC

The N_2/H_2 mixture is fed into the anode compartment of the cell. When DC power is supplied to the cell electrodes, the H_2 in the gaseous mixture reacts with hydroxyl ions (OH^-) in the electrolyte to form water and electrons. The equation for the anode half-cell reaction is:

$$H_2 + 2OH^- = 2H_2O + 2e^- \qquad (1)$$

At the cathode, the electrons react with water in the electrolyte to form H_2 and OH^-. The equation for the cathode half-cell reaction is:

$$2H_2O + 2e^- = H_2 + 2OH^- \qquad (2)$$

The OH^- migrate from the cathode to the anode under the electromotive force provided by the power supply for reaction with more H_2. The H_2-depleted N_2/H_2 stream at the anode and the H_2 generated at the cathode exit through the exhaust manifolds of the cell.

Although the overall electrochemical reaction neither consumes nor generates water, water must be supplied to the cell to maintain the electrolyte level between the electrodes. The N_2/H_2 feed is dry and the product N_2 and H_2 streams leave the cell in approximate equilibrium with the water vapor pressure above the electrolyte within the cell. The additional water required to humidify the product gas streams is fed into the cell by a static water vapor feed mechanism. The internal water cavity is separated from the cathode compartment by an electrolyte matrix. The concentration of electrolyte in the water feed cavity is initially at the same concentration as the electrolyte within the cell matrix. As water is removed from the cell electrolyte to humidify the product gas streams, the electrolyte concentration increases (i.e., the concentration of water within the electrolyte decreases). The difference in concentrations between the electrolyte in the water feed cavity and cell matrix causes water to evaporate from the water feed cavity and transfer to the cell matrix.

Since the theoretical cell voltage for the electrochemical reactions is zero, all power required by the electrochemical cell is dissipated as waste heat. Heat removal, therefore, must be provided to maintain a constant cell operating temperature. The cell design provides for internal liquid cooling. A coolant cavity adjacent to the current collector separating the coolant and anode cavities is used to manifold cooling water through the cell.

System Design Features

The following features were incorporated into the system design:

1. The system provides for automatic one-button startup and one-button shutdown.
2. The system is designed for a N_2 delivery rate of 6.81 kg/d (15 lb/day).
3. The N_2/H_2 separation process is carried out in three stages with 85% of the feed H_2 removed in the polymer first stage, and 13% and 2% removed in the electrochemical second and third stages, respectively.

4. The electrochemical stages are combined into a single module containing eight cells in the second stage and one cell in the third stage.
5. The electrochemical third stage operates at a constant voltage with third stage current indicating H_2 concentration levels.
6. Second stage current and hence H_2 removal rate is controlled as a function of third stage current (i.e., H_2 concentration) to give the subsystem a H_2 removal capacity of the design point ±20%.
7. The electrochemical module contains internal humidifiers to meet gas humidification requirements.
8. Instrumentation is maintainable and is divided into two packages: Control and Monitor.
9. The system provides for automatic, fail-safe shutdown to protect the system when critical parameters exceed tolerance levels.
10. The system automatically depressurizes on shutdown.
11. Automatic, fail-safe N_2 purge is provided during startup and shutdown.
12. The system has five modes of operation: NORMAL, SHUTDOWN, PURGE, VENT, and WATER FILL.
13. The Control Instrumentation provides overrides on all valves, the coolant pump, and electrochemical cell power.

System Operation

Figure 5 is a schematic of the Polymer-Electrochemical N_2/H_2 Separator System. It shows the functional location of all system components.

The N_2/H_2 gas mixture at an elevated pressure is manifolded into the Polymer Diffusion Unit through SV-1. The temperature of the gas stream is monitored to protect the Polymer Diffusion Unit from damage caused by high gas temperature. The Polymer Diffusion Unit must be operated at temperatures less than 323K (122F). The H_2-depleted N_2 stream from the Polymer Diffusion Unit is then manifolded to the Electrochemical N_2/H_2 Separator.

In the Electrochemical N_2/H_2 Separator, the remaining H_2 in the N_2 product stream is removed. The N_2 product stream pressure is controlled above the H_2 side pressure in the electrochemical module by a differential pressure regulator (DPR1). The differential pressure level of the N_2 product stream is monitored using a differential pressure transducer (DP1). The N_2 product stream exhausts the system for use or is vented through a three-way solenoid valve (SV5). A flow sensor is provided on the N_2 product stream for use during startup sequencing to signal the application of power to the electrochemical module. If power were applied before N_2/H_2 gas mixture reached the electrochemical module, the lack of

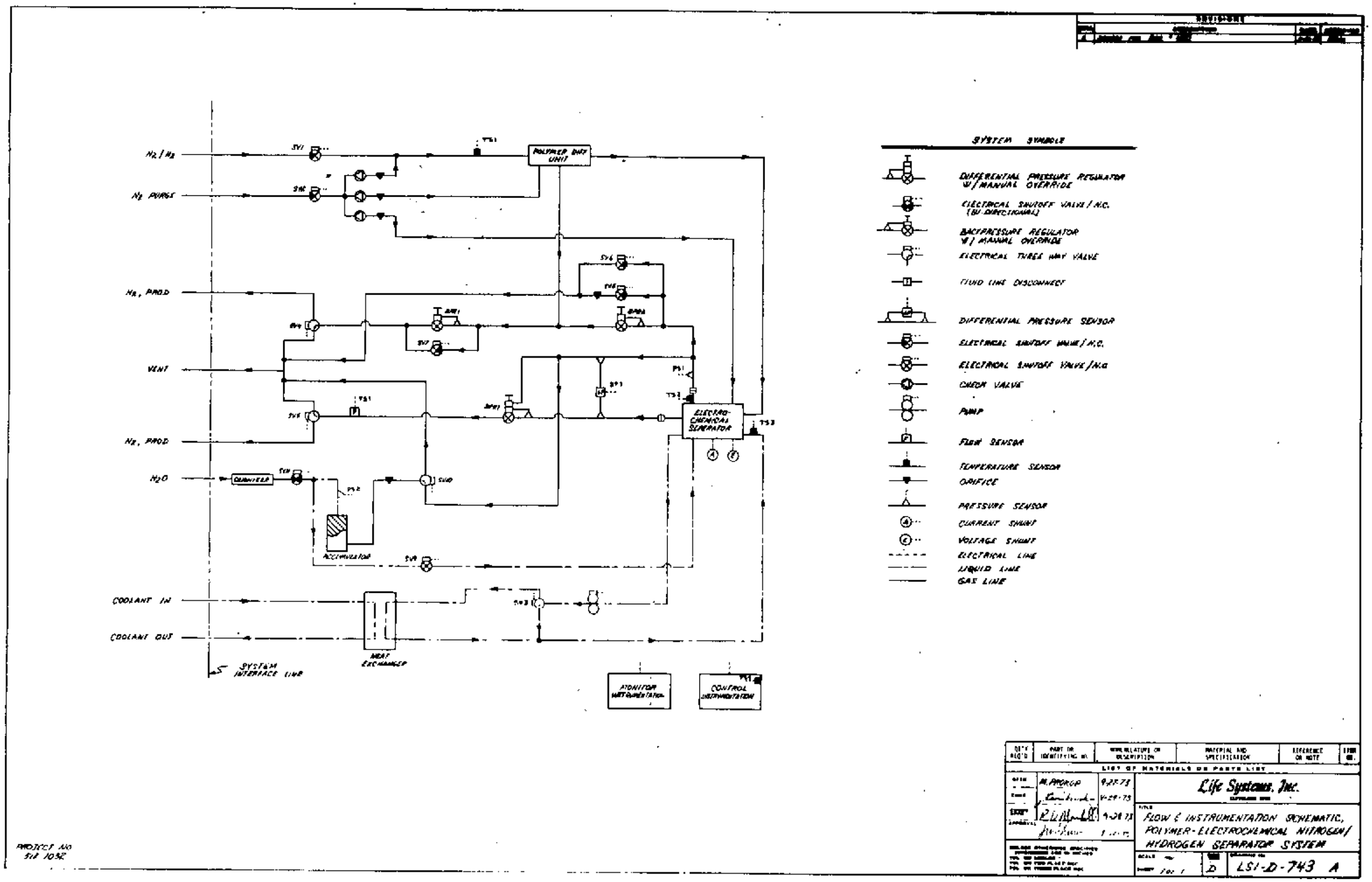

FIGURE 5 POLYMER-ELECTROCHEMICAL N_2/H_2 SEPARATOR SYSTEM SCHEMATIC

H_2 would cause high cell voltage in the second stage cells and result in a high voltage shutdown.

The H_2 product streams from the Polymer Diffusion Unit and the Electrochemical N_2/H_2 Separator are joined together and exhaust the system through a three-way solenoid valve (SV4). The H_2 product gas pressure is controlled by a backpressure regulator (BPR1). A solenoid valve (SV7) is provided to bypass BPR1 during automatic system purging. The H_2 product stream pressure from the electrochemical module is maintained at a higher level than the system H_2 product pressure by a backpressure regulator (BPR2). Regulator BPR2 actually controls the absolute pressure level of the Electrochemical N_2/H_2 Separator and the N_2 product pressure through DPR1. Two solenoid bypass valves (SV6 and SV8) for BPR2 are used during system shutdown sequencing. Solenoid valve SV8 is used in conjunction with an orifice to slowly depressurize the electrochemical module upon shutdown. After system depressurization, SV6 is used for purging. The pressure of the electrochemical H_2 product stream is monitored by a pressure transducer (PS1). The temperature sensor in the electrochemical H_2 product stream (TS2) is used to indicate electrochemical module temperature.

A liquid coolant loop is used to control the temperature of the Electrochemical N_2/H_2 Separator. Coolant is circulated through the module and the coolant temperature is monitored and used to control the temperature of the separator. The heat is removed from the circulating coolant loop through a heat exchanger. Solenoid valve SV3 is used to divert flow through this heat exchanger or bypass it to maintain a preset temperature level in the electrochemical module.

Water used by the electrochemical module is fed through a deionization cartridge and solenoid valve (SV11) to a water feed accumulator. The accumulator is pressure referenced to the electrochemical H_2 product pressure. As water is removed from the cell water feed cavity, it causes a decrease in the cavity pressure which forces water from the accumulator into the cells. Periodically, the accumulator is refilled by closing SV9, depressurizing the accumulator through SV10, and opening SV11. An orifice is provided in the H_2 vent line so that depressurization and repressurization does not take place too rapidly and cause a differential pressure spike in either the accumulator or the Electrochemical N_2/H_2 Separator.

Nitrogen purge for the system is controlled by a solenoid valve (SV2). The purge is divided into three separate streams. Even flow distribution is provided by three calibrated orifices.

Control and Monitor Instrumentation Design

The control and monitor instrumentation is the equipment required to control system parameters and to provide protective monitoring of the system parameters. The electronics for the polymer-electrochemical N_2/H_2 Separator were designed as two separate units, one for control and one for monitoring. The operation of these two units is as independent as possible. Interconnections between the control, the monitoring, the ground support, and the system are via cables and connectors for ease in assembly and maintenance. The control and monitoring chasssis are mechanically constructed such that they may be installed in separate instrument cases or in a standard 19" relay rack cabinet with the groupd support equipment. In addition to the two electronic units, there are sensors in the system which provide parameter signals for use in the control and monitor instrumentation.

Control Instrumentation

The control instrumentation provides the circuits which control (a) system startup and shutdown sequences, (b) module temperature, and (c) electrochemical module power. The system was designed for automatic one-button start, one-button stop operation. To provide off-design and manual operation capability, the control instrumentation contains override switches on its back panel.

Sequence Control Logic. The sequence control logic determines the on-off operation of Stage 2 and Stage 3 currents, the cooling pump, and the system's solenoid valves for each of the operating modes and during mode transitions. The system operating modes are presented in Table 2. There are two steady-state operating modes; the STOP mode in which the equipment is not performing its intended function but is powered, and the NORMAL mode in which the equipment is performing its intended function and operating normally. In addition, there are three transient modes: (1) the WATER FILL mode, (2) the VENT mode, and the PURGE mode. The WATER FILL mode occurs once approximately every 24 hours as determined by an automatic timer in the system. It lasts only long enough to fill the water tank, at which point the system will revert to the NORMAL operating mode again. The VENT mode is called for whenever Stage 3 operates at a constant current. The constant current operation occurs when the H_2 concentration in the N_2 product gas entering Stage 3 is too high. Hydrogen-contaminated N_2 product gas is then vented through SV4 and SV5. If the VENT mode continues for an excessive period of time, as determined by an internal timer, the system will automatically sequence to the STOP mode. The PURGE mode is called for during the startup and shutdown mode change sequences. The PURGE mode consists of operating the appropriate solenoid valves to allow N_2 to purge the system. This mode is only in effect for two minutes during a startup sequence and for two minutes during a shutdown sequence. A detailed description of these mode transition sequences is presented in Appendix 1.

Module Temperature Control. Figure 6 is a block diagram showing the configuration of the control system which maintains the electrochemical module at the desired temperature by on-off operation of three-way solenoid valve (SV3). Solenoid valve SV3 determines whether the liquid coolant flows through a liquid-to-liquid heat exchanger or bypasses it.

Module temperature is monitored with a thermistor. This signal is conditioned by the temperature control logic and compared with a manual temperature set signal. The manual temperature set signal is provided by a digital potentiometer located on the back panel of the control chassis. The difference between these two signals is used to control the solenoid valve driver circuit which in turn operates solenoid valve SV3. When solenoid valve SV3 is deenergized, the coolant flows through the heat exchanger to remove heat and lower the module temperature.

TABLE 2 POLYMER-ELECTROCHEMICAL N_2/H_2 SEPARATOR SYSTEM OPERATING MODES

Controlled Item	Steady-State				Transient					
	Stop		Normal		Water Fill		Vent		N_2 Purge	
	On	Off	On	Off	On	Off	On	Off	On	Off
Stage 2 Current		X	X		X		X			X
Stage 3 Current		X	X		X		X			X
Coolant Pump		X	X		X		X		X	
Solenoid Valves(a)										
SV1		X	X		X		X			X
SV2		X		X		X		X	X	
SV3(b)	← As Required →									
SV4		X	X		X			X		X
SV5		X	X		X			X		X
SV6		X		X		X		X	X	
SV7		X		X		X		X	X	
SV8		X		X		X		X		X
SV9		X		X	X			X		X
SV10		X		X	X			X		X
SV11		X		X	X			X		X

(a) For solenoid valves, Off = Deenergized, On = Energized.
(b) SV3 is operated by the temperature control circuit which is independent of the operating mode.

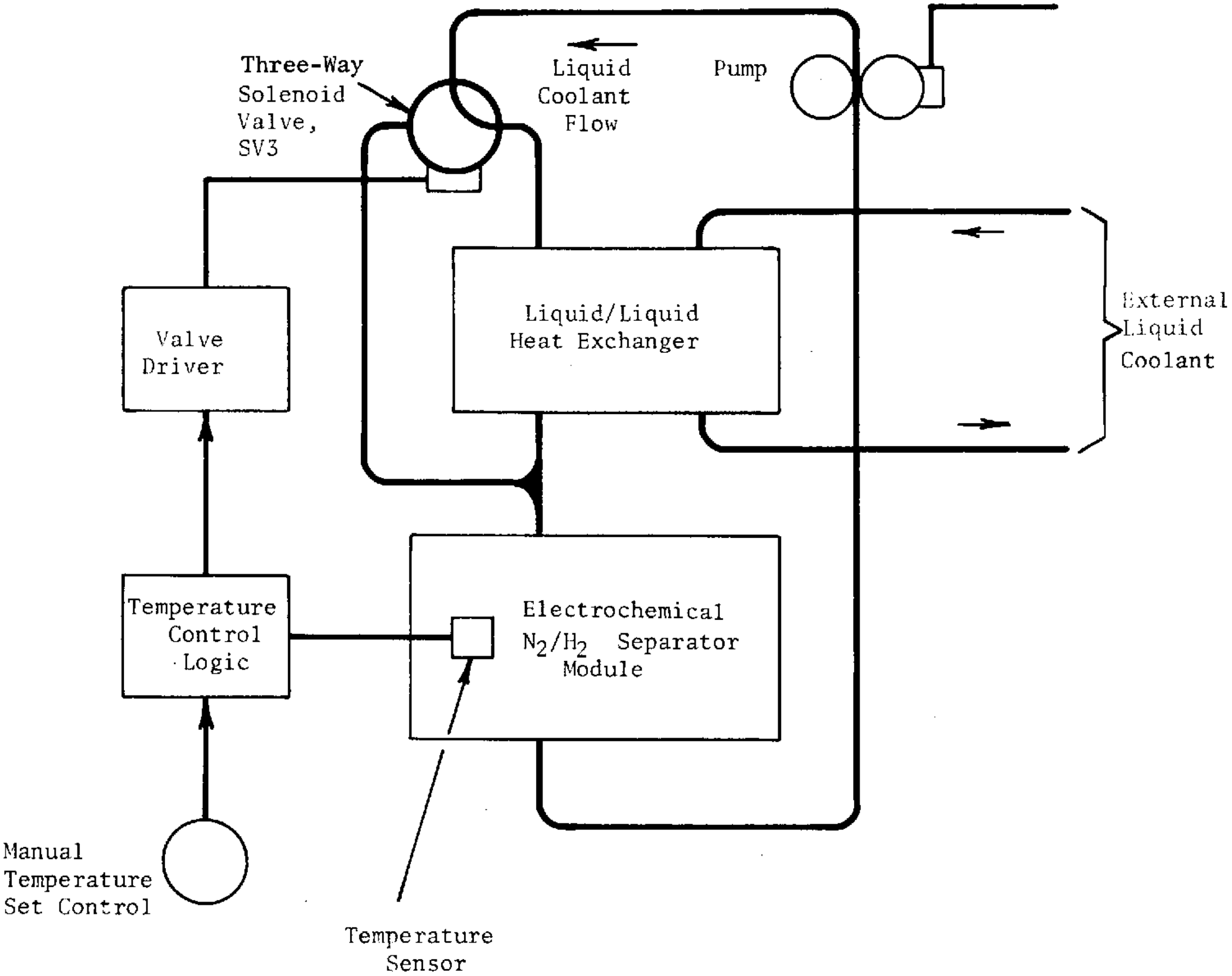

FIGURE 6 MODULE TEMPERATURE CONTROL BLOCK DIAGRAM

When solenoid valve SV3 is energized, the coolant bypasses the heat exchanger and no heat is removed. Since the module is generating heat, its temperature and the coolant temperature will increase. Note that this solenoid valve is not controlled by the sequence control logic mode and operates as described above whenever the electronics system has power supplied.

Module Power Control. Both Stage 2 and Stage 3 module currents are provided by switching regulators. This type of regulator produces very efficient power conversion and has operated at efficiencies greater than 80%.

Stage 3 Current Control. Stage 3 of the electrochemical module is normally operated at a constant voltage. Figure 7 is a block diagram of the power control scheme for Stages 2 and 3. Stage 3 cell voltage is monitored, conditioned, and compared to a set point signal by the control logic. The error signal (i.e., the difference between the set point and cell voltage signals) is used to control the pulse width modulator. The pulse width modulator turns the power switch transistors on and off at a fixed rate with a duty cycle (on time relative to total period) that varies according to the error signal. An increase in the error signal causes an increase in the duty cycle, which increases the Stage 3 current (I_3). Similarly, a decrease in the error signal causes a decrease in the duty cycle and will decrease I_3. The effect of this feedback control is that I_3 is increased or decreased to maintain essentially zero error between the Stage 3 voltage signal and the voltage set point signal to control Stage 3 voltage at the set value.

The chopped or pulsating current generated by the power switch transistors is filtered to produce a smooth DC current for Stage 3. This current passes through a current measuring shunt to Stage 3 of the electrochemical module. The current signal is conditioned by the control logic and compared to a current set point signal. The amount of current required by Stage 3 to maintain the desired constant voltage will vary between zero and this set current. When the current tries to increase above the set level, the control reverts to a constant current control and the voltage will then vary between zero and the set voltage level with no appreciable change in current. Figure 8 is a graph of the current/voltage relationship for a voltage set point set at 0.5V and a current set point set at 21A.

The amount of current required by Stage 3 to maintain the desired constant voltage is directly proportional to the amount of H_2 in the N_2 product stream. Stage 3 is therefore used as a sensor to determine the purity of N_2 being generated. If the current required by Stage 3 to maintain the desired constant voltage reaches the current set point, the sequence control logic will command the VENT mode. If this condition exists for a long enough period of time (as determined by a timer in the sequence control logic), shutdown sequence will be commanded. If the H_2 level drops so that Stage 3 returns to the normal range of operation at a constant voltage, the sequence control will return the system to the NORMAL operating mode and reset the timer.

Stage 2 Current Control. The module is constructed such that the negative side of Stage 3 is electrically connected to the positive side of Stage 2. This

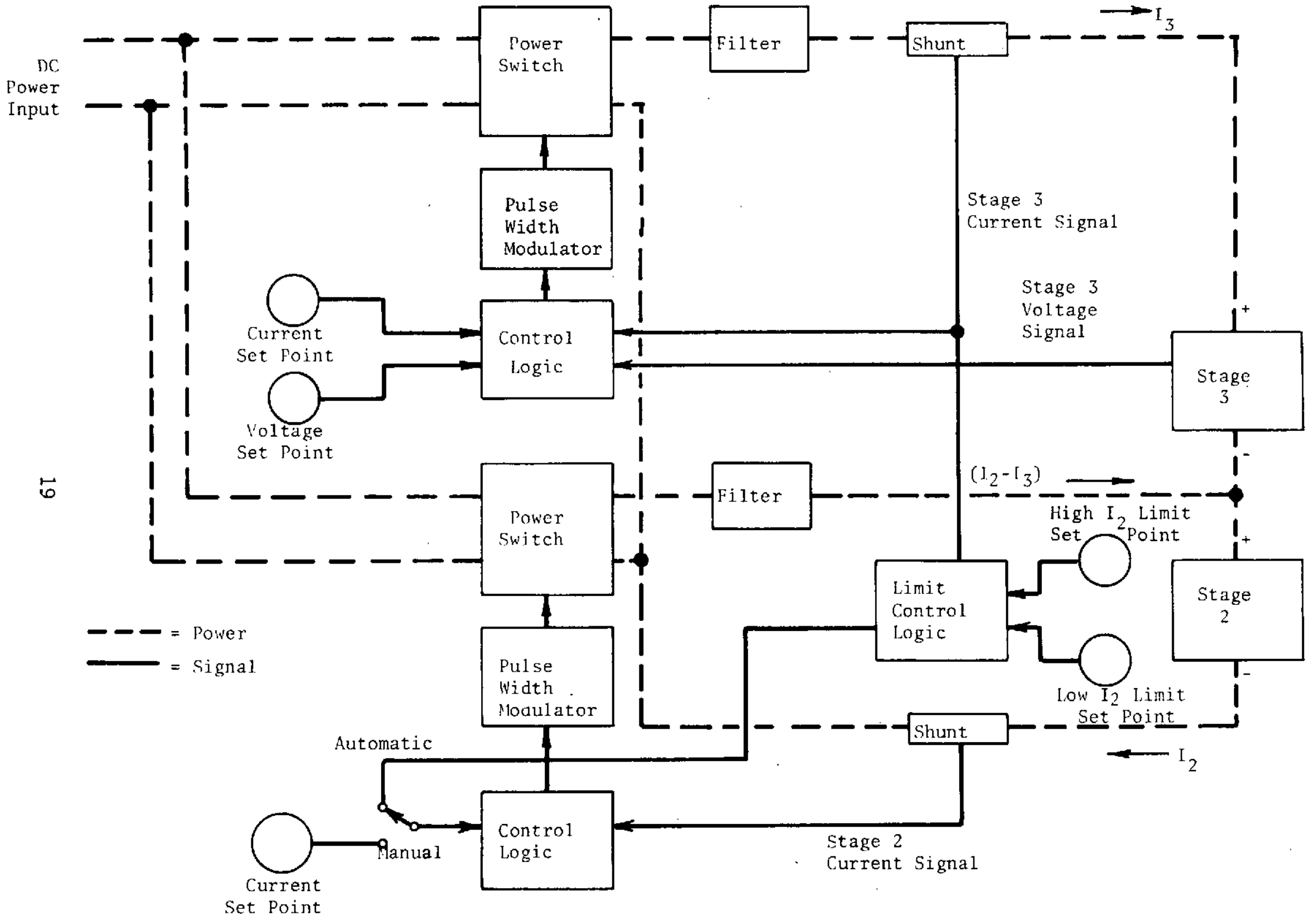

FIGURE 7 POWER CONTROL BLOCK DIAGRAM

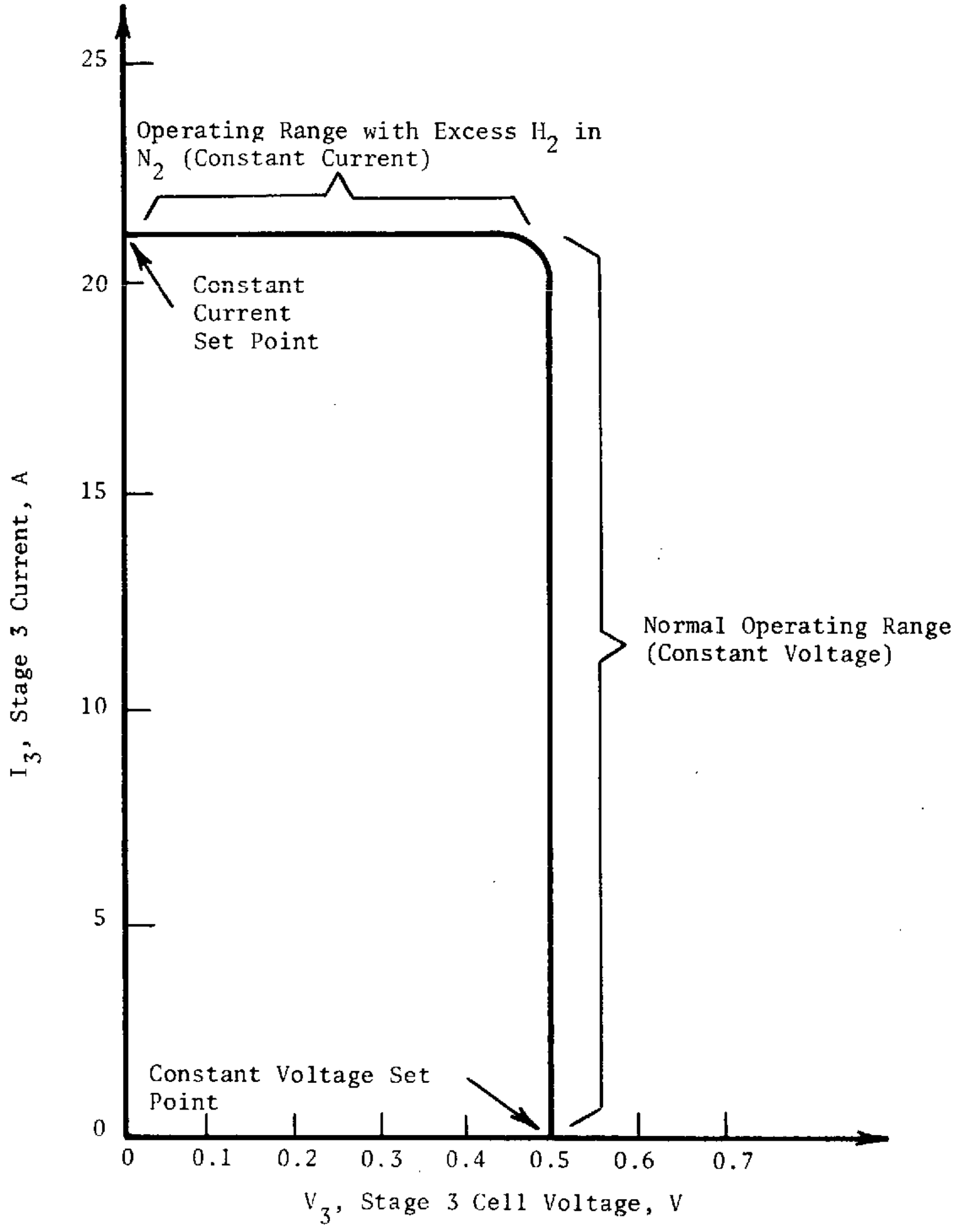

FIGURE 8 STAGE 3 CURRENT/VOLTAGE RELATIONSHIP

configuration allows the current flowing through Stage 3 to also flow through Stage 2 as shown in Figure 7. The power switching transistors and filter for Stage 2 provide the difference in current between the current required for Stage 2 (I_2) and I_3. The current passing through Stage 2 is measured by a shunt and the signal fed to the Stage 2 control logic. The signal is conditioned and compared to a current set point signal. The current set point signal for Stage 2 can be either a manual signal from a digital potentiometer on the back panel of the controller or a function of I_3. Selection between these two is made by the manual/automatic switch adjacent to the manual current set point potentiometer on the back panel. Regardless of which signal provides the current set point, the I_2 signal is compared to the set point signal and an error signal is generated. As in the Stage 3 control, this error signal is used to control the output current through the pulse width modulator, power switch, and filter. The automatic mode current set signal is derived by passing the I_2 signal through signal shaping logic which sets the low and high current limits as well as the slope between these two limits.

Figure 9 shows the relationship between I_2 and I_3 for the automatic mode. The slope (change in I_2 with respect to a change in I_3) of this relationship in the linear range is adjustable. Similarly the upper and lower current limit set points are setable with printed circuit (PC) card potentiometers.

Override Switches. The back panel of the control instrumentation package contains 13 three-position switches. These switches allow for two modes of operation for I_2 and I_3, coolant pump, and all solenoid valves. The automatic position allows the sequence control logic to automatically control the on and off functions of the particular item. The remaining two positions of each switch allow for a manual override control. One position provides manual off (deenergized) operation, the other position provides manual on (energized) operation. Since these switches are mounted on the back panel of the instrumentation package, front panel override indication is provided. Should any of the 13 switches be placed in either of the two manual override positions, the amber override light on the start/ override switch will be illuminated.

The controls were designed and constructed such that the system will operate automatically with the only manual operations required being the operation of a single START pushbutton to turn the system on and a single STOP pushbutton to turn the system off. The manual override switches and current and voltage set point controls were included to allow manual operation of the system during off design and parametric testing. They are not normally used and as such are located on the back panels.

Monitor Instrumentation

The monitor instrumentation consists of the monitoring and display electronics for two pressures (module differential and system), four temperatures (module, gas supply, coolant, and electronics), cell voltages, and H_2 contamination. A basic element of this monitoring instrumentation system is the PC card which contains signal conditioning, level detectors, storage, lamp drivers, and logic. A block diagram of this commonality monitoring PC card is shown in Figure 10. Wherever possible, PC cards previously developed by LSI for use in other life support systems were used in this system.

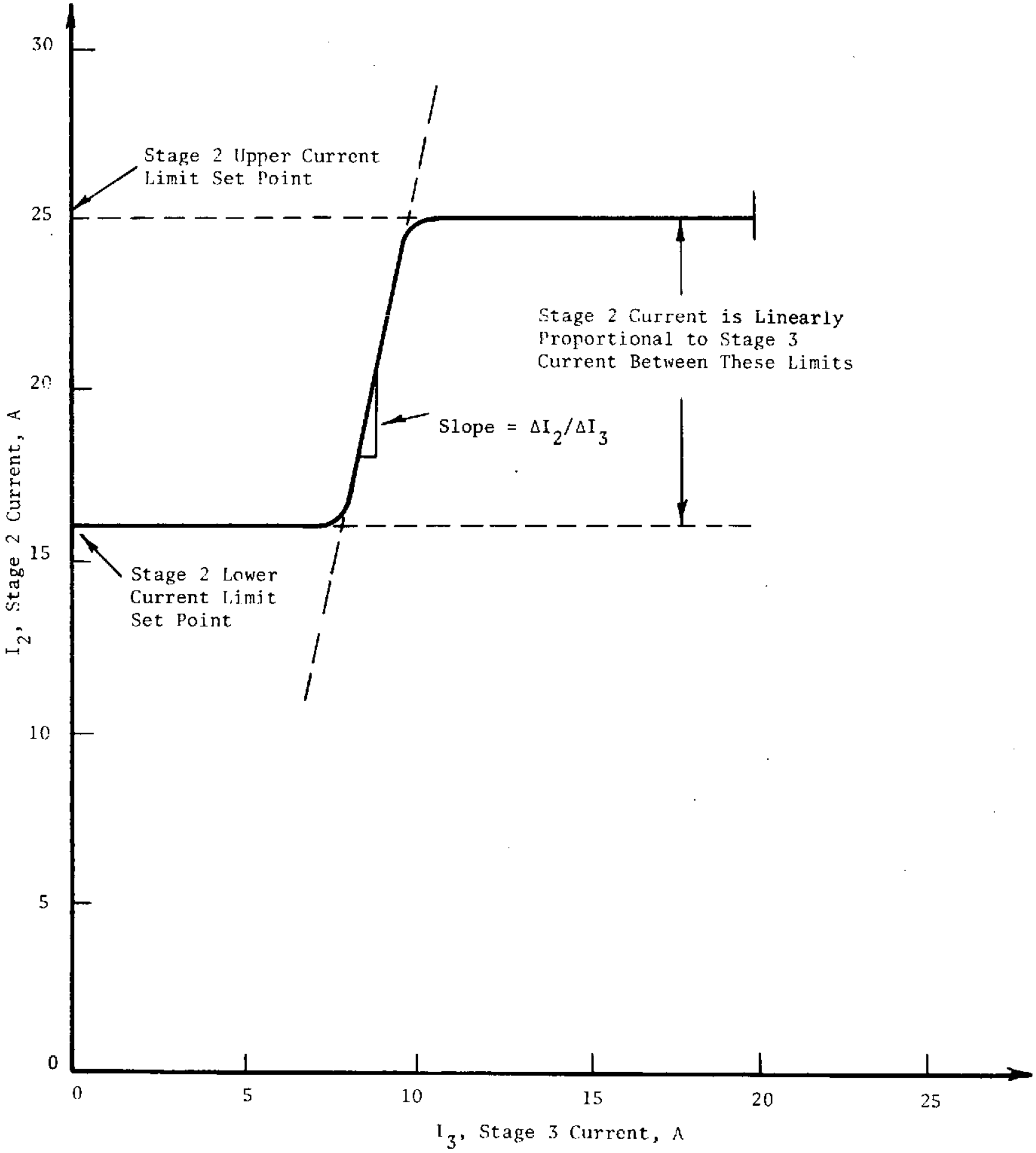

FIGURE 9 STAGE 2 AUTOMATIC CURRENT CONTROL

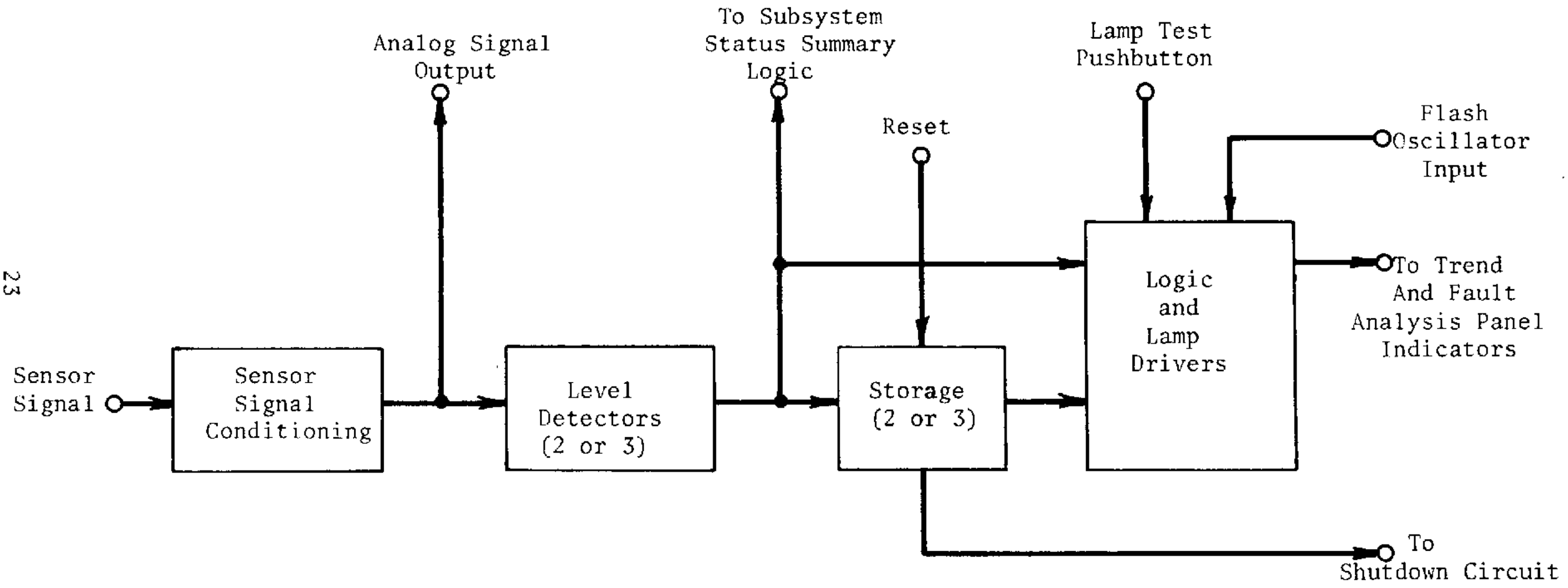

FIGURE 10 MONITOR INSTRUMENTATION PC CARD BLOCK DIAGRAM

A typical monitoring card accepts a sensor input signal and conditions it to a standard 0-5 VDC level. This conditioned analog signal is available for readout by ground support equipment. The 0-5 volt signal is digitized on the card into three or four ranges by two or three level detectors. The parameter being processed determines whether three or four ranges will be used.

When the parameter monitored is in its normal range, none of the level detectors is tripped and a green indicator light is illuminated. If the parameter moves out of its normal range, it will trip the first level detector which turns out the green indicator and turns on an amber indicator. The parameter is now in the caution range. If the parameter moves further from its normal range, it will trip the second level detector which will turn out the amber indicator and light a flashing red indicator. The parameter is now in the third, or warning range. If the parameter should continue to move away from normal, it will finally reach the fourth range by tripping the third level detector. This will turn out the flashing red indicator and light a red indicator. This fourth range is the alarm range. Any signal which trips the third level detector will also send a shutdown signal to the control system.

The third level detector which provides the alarm range and the shutdown signal is the one that may or may not be included on a particular monitoring PC card. If the parameter monitored is a safety critical one from a point of view of personnel or equipment safety, the PC card will include this fourth range. If the parameter is monitored for trend or fault analysis information, only three ranges and two level detectors are used.

The shutdown signal from each monitor PC card is connected through a manual switch to the shutdown bus. If any monitor PC cards go into the alarm range, the shutdown bus will carry this information to the control electronics and initiate a shutdown sequence. Manual override switches are provided to allow any one or more monitoring PC cards to be disconnected from the shutdown bus. Override capability allows system operaion at off-design or out-of-tolerance conditions without causing a shutdown. During normal system operation all switches are closed and the overrides are not used.

The PC monitoring cards contain logic and memory which allow both the present level and the previously obtained highest level to be displayed simultaneously on the indicator lamps. A reset input on each card allows the stored information to be cleared from the memory when desired. This reset input is connected to a manually operated pushbutton on the Performance Trend and Fault Analysis Panel.

A lamp test input is provided to each monitoring PC card which allows all the indicator lamps connected to the cards to be tested. This input on all cards is connected to a second pushbutton on the Performance Trend and Fault Analysis Panel.

In addition to the standard monitoring card discussed above, three auxiliary circuits are required. The first is the oscillator necessary to operate the flashing red lights for each of the monitoring PC cards. The second circuit collects the present level information from each of the monitoring PC cards, summarizes them, and lights a green, amber, flashing red or red light. The light lit at any time represents the highest present level of any of the monitoring PC cards in the system. The third is the cell voltage scan. The module contains eight cells in Stage 2 and each cell voltage is monitored individually. A total stage voltage monitor is not sufficient since one cell can exceed the desired limit without noticeably affecting total stage voltage. A relay scanning system is used to look at each of the cells in the module one at a time. The logic which is used to sequence the scan relays also contains the logic circuits required to drive the seven segment, light-emitting diode (LED) cell counter display which is mounted on the Performance Trend and Fault Analysis Panel. The cells are scanned sequentially and the LED indicator shows which cell is being examined.

Sensors

Sensors are used throughout the system to convert various physical parameters to electrical signals. They are used for both control and monitoring functions. Table 3 lists all the system sensors, their type, range, and use.

Control Sensors. There are three sensors used for system control, two exclusively for control and a third for both control and monitoring. Pressure sensor PS2 senses the water tank pressure. When the water tank pressure reaches the pressure set on the switch, a contact switch closes signalling the water fill sequence to terminate the filling.

Flow sensor FS1 senses N_2 product gas flow and consists of two thermistors which are electrically heated to the same temperature. One thermistor is located such that N_2 flow will increase its convective cooling rate and reduce its temperature. The second thermistor is located such that the N_2 flow will not cool it, but is located close to the first thermistor so that any ambient variations will be seen by both thermistors and will be effectively cancelled. The difference in temperature between the two thermistors is measured by a bridge circuit in the control electronics. The magnitude of this temperature difference is a direct measure of the N_2 flow rate through the system. This signal is used in the sequence control circuits.

The third sensor used is the coolant temperature sensor TS3. Temperature sensor TS3 is a single thermistor which is used to monitor coolant temperature and becomes the feedback signal to the temperature control electronics.

Monitor Sensors. Six sensors are used for system parameter monitoring, five exclusively for monitoring and one in conjunction with control as described above. The signal from TS3 (conditioned in the control electronics) is fed to the monitor instrumentation for trend and fault analysis and shutdown protection. The monitor instrumentation uses a transducer monitor PC card for this because it does require signal conditioning on it.

Temperature sensor TS1 monitors gas supply temperature, temperature sensor TS2 monitors module temperature, and temperature sensor TS4 monitors the control electronics temperature. All three are thermistors. Each sensor connects to a temperature monitoring PC card with signal conditioning, trend and fault analysis, and shutdown protection.

TABLE 3 POLYMER-ELECTROCHEMICAL N_2/H_2 SEPARATOR SYSTEM SENSORS

Parameter	Ref. No.[(a)]	Range	Type	Use
Module Differential Pressure	DP1	0 to 172 kN/m^2 (0 to 25 Psid)	Bridge Transducer	Monitor
System Pressure	PS1	0 to 1725 kN/m^2 (0 to 250 Psia)	Bridge Transducer	Monitor
Water Tank Pressure	PS2	104 to 1484 kN/m^2 (15 to 215 Psia)	Pressure Switch	Control
N_2 Flow	FS1	0 to 15 dm^3/min (Slpm)	Two Heated Thermistors	Control
Gas Supply Temperature	TS1	294 to 377K (70 to 220F)	Thermistor	Monitor
Module Temperature	TS2	294 to 377K (70 to 220F)	Thermistor	Monitor
Coolant Temperature	TS3	294 to 377K (70 to 220F)	Thermistor	Control and Monitor
Electronics Temperature	TS4	294 to 377K (70 to 200F)	Thermistor	Monitor

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(a) Reference designation number as shown on system schematic, LSI-D-743A, Figure 5.

There are two pressure transducers in the system. The first, DP1, is used to monitor the differential pressure across the module and is a bridge type transducer with internal signal conditioning which provides a 0-5V DC output. The second system pressure transducer, PS1, is also a bridge type with internal signal conditioning. These two transducers are used exclusively for monitoring instrumentation purposes. Each is fed to a transducer monitor PC card.

Hardware Description

The Polymer-Electrochemical N_2/H_2 Separator System consists of 38 components of 17 different types. A list of the components by type is given in Table 4. A short functional description of the components follows.

1. Polymer Diffusion Unit - the Polymer Diffusion Unit separates 80-85% of the feed H_2 from the N_2/H_2 feed gas stream. The N_2/H_2 feed is at 1035 kN/m^2 (150 psia) and H_2 is collected at 172 kN/m^2 (25 psia). The unit consists of hollow polyester fibers in a tube bundle attached at each end to a manifold plate using an epoxy resin. Figure 11 is a photograph of the Polymer Diffusion Unit.

2. Electrochemical Module - The electrochemical module consists of nine cells and removes the remaining H_2 in the N_2/H_2 exhaust from the Polymer Diffusion Unit. Both the N_2 and H_2 product gases are maintained at the same pressure, approximately 1035 kN/m^2 (150 psia). The separation takes place in two stages (i.e., Stage 2 and 3 in the H_2 separation process) having eight cells and one cell, respectively. The stages are combined into a single module with the gases manifolded between stages internally. Figure 12 is a photograph of the Electrochemical N_2/H_2 Separator module. Figure 13 shows the individual cell parts. The module-cell component characteristics are listed in Table 5.

3. Backpressure Regulators - There are two backpressure regulators in the system. One regulates the H_2 product pressure in the electrochemical module from 103-1829 kN/m^2 (15-265 psia). The second regulates system H_2 delivery pressure from 103-449 kN/m^2 (15-65 psia). Both regulators are preset for automatic operation and can be adjusted manually for off-design operation. The regulators are located on the panel of the mechanical components assembly package as shown in Figure 14.

4. Differential Pressure Regulator - The differential pressure regulator controls the N_2-to-H_2 differential pressure from 0-345 kN/m^2 (0-50 psid) in the electrochemical module. The regulator is preset during automatic operation and can be adjusted manually for off-design operation from the front panel of the mechanical components assembly.

5. Solenoid Valves - The system contains 11 solenoid valves, 10 of which are used for operating mode transitions and one (SV3) which is used in the temperature control loop. The solenoid valves use 28 VDC power. The operation of the valves is fully automatic, however, manual override switches for each valve are provided on the back of the control instrumentation package. A typical solenoid valve is shown in Figure 14.

TABLE 4 POLYMER-ELECTROCHEMICAL N_2/H_2 SEPARATOR SYSTEM COMPONENTS

Component	No. Required
Diffusion Unit, Polymer	1
Module, Electrochemical	1
Regulator, Backpressure	2
Regulator, Differential Pressure	1
Valve, Solenoid	
Normally Open	1
Normally Closed	6
Three-Way	4
Heat Exchanger, Liquid Coolant	1
Pump, Liquid Coolant	1
Accumulator, Water	1
Cartridge, Deionization	1
Flow Restrictor	5
Valve, Check	3
Sensor, Pressure	2
Sensor, Differential Pressure	1
Sensor Temperature	4
Sensor Flow	1
Instrumentation, Control	1
Instrumentation, Monitor	1

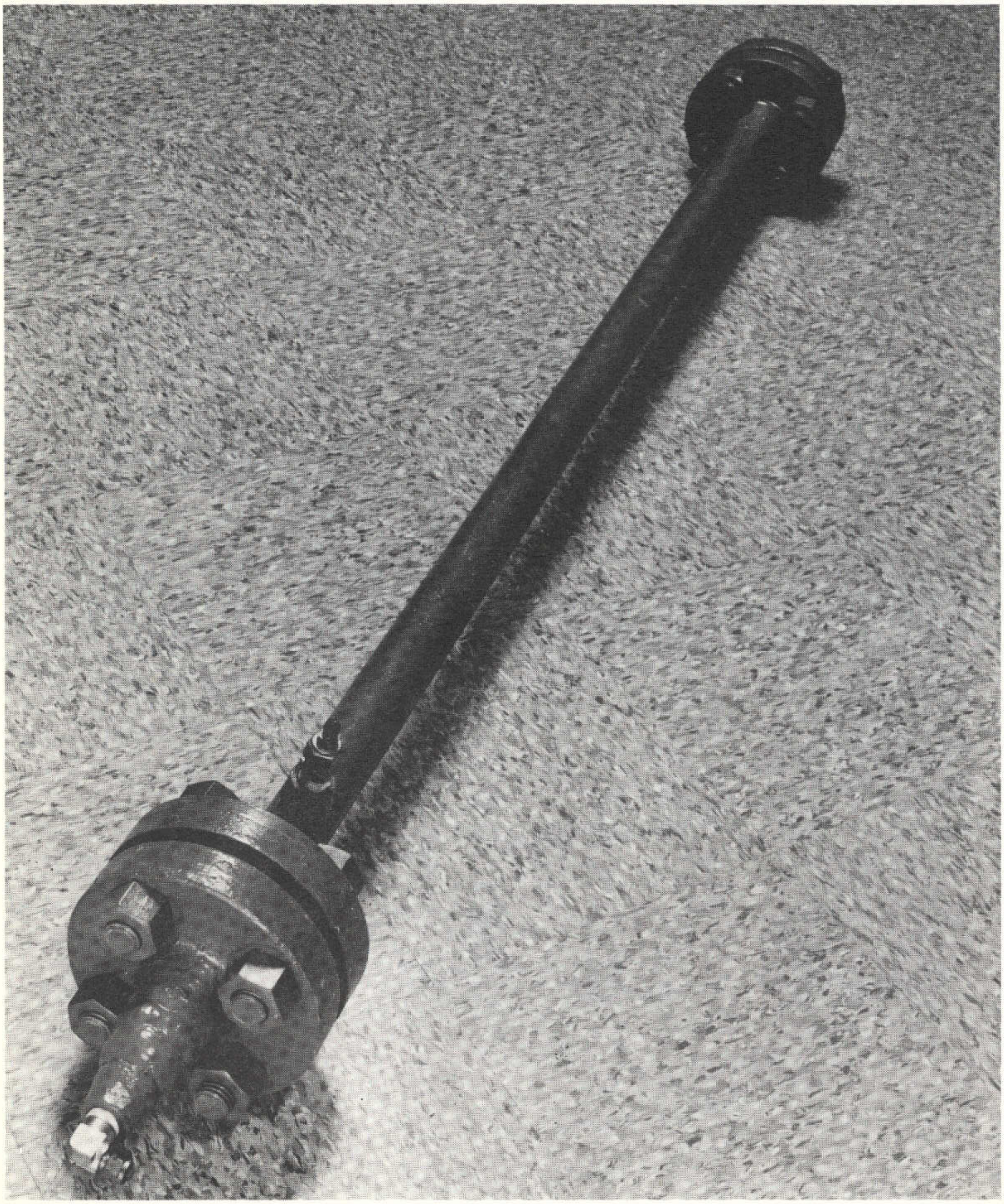

FIGURE 11 POLYMER DIFFUSION UNIT

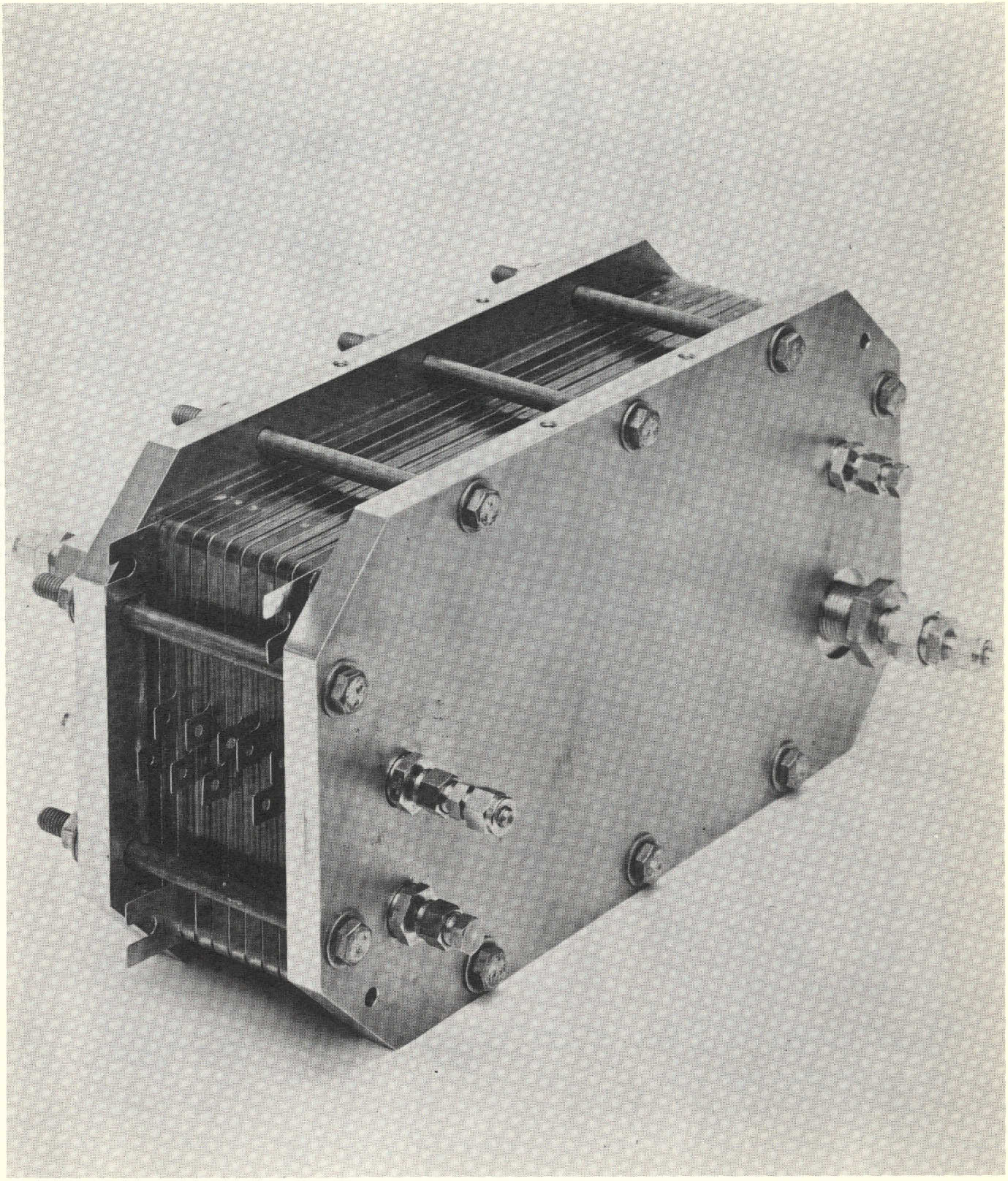

FIGURE 12 ELECTROCHEMICAL N_2/H_2 SEPARATOR MODULE

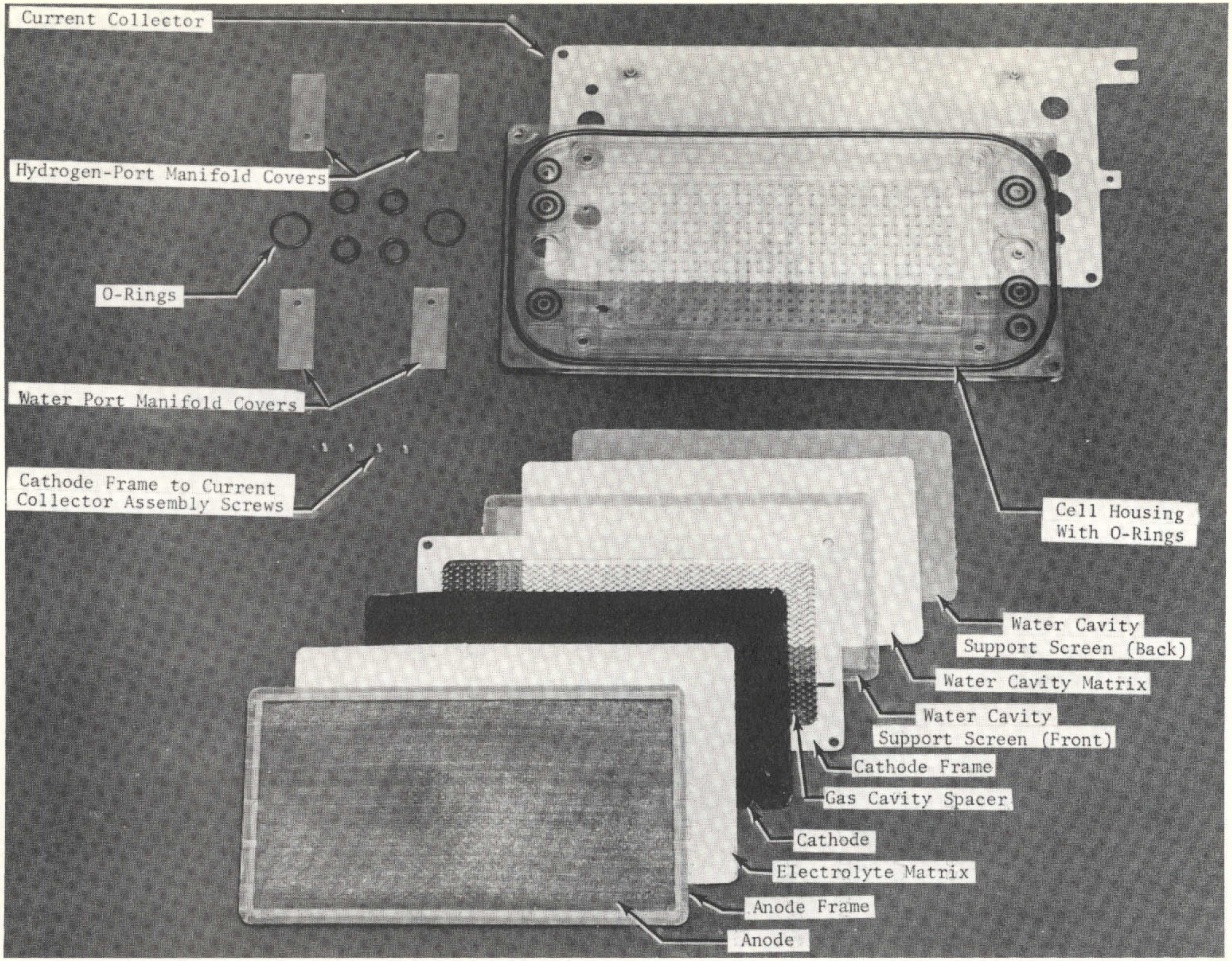

FIGURE 13 ELECTROCHEMICAL N_2/H_2 SEPARATOR CELL PARTS

TABLE 5 ELECTROCHEMICAL N_2/H_2 MODULE CELL CHARACTERISTICS

Cell Housing	Polysulfone
Anode Frame	Polysulfone
Cathode Frame	Nickel
Gas Cavity Spacers	Nickel
Current Collectors	Nickel
O-Rings	Ethylene Propylene
Endplates	Stainless Steel
Insulation Plates	Polysulfone
Electrolyte Matrix	LSI Proprietary
Matrix Thickness, cm (In)	0.038 (0.015)
Electrodes	LSI Proprietary
Electrode Area, cm^2 (Ft^2)	223 (0.24)
Electrode Thickness, cm (In)	0.013 (0.005)
Electrolyte	25% KOH
Water Cavity Matrix	LSI Proprietary
Water Cavity Support Screens	Teflon

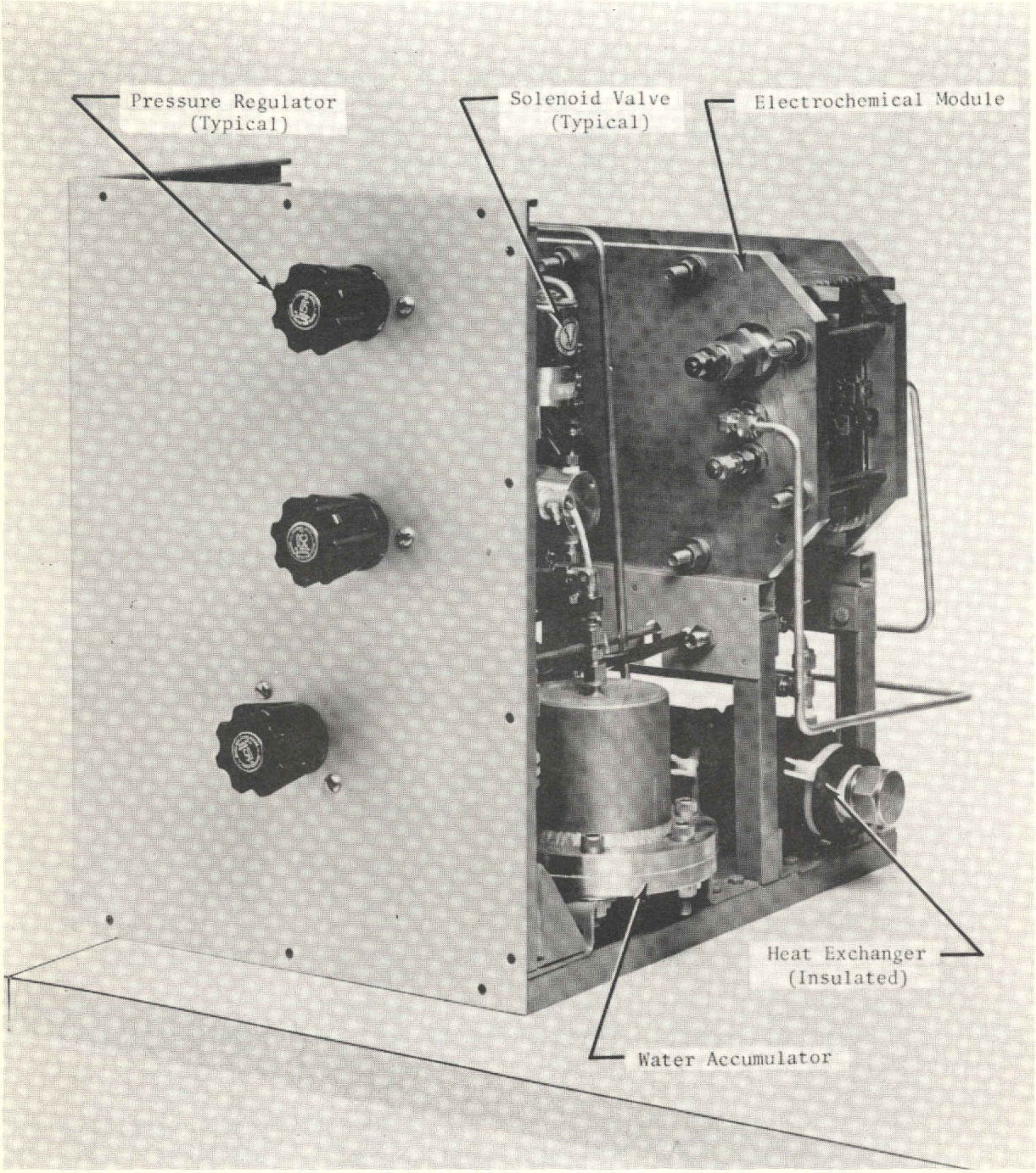

FIGURE 14 MECHANICAL COMPONENTS ASSEMBLY

6. Heat Exchanger - The liquid coolant heat exchanger removes waste heat generated by the electrochemical module by cooling the circulating liquid coolant loop that flows through the module. Heat is exchanged between the module liquid coolant and refrigerated liquid coolant in this liquid-to-liquid type heat exchanger.

7. Liquid Coolant Pump - The liquid coolant pump circulates coolant through the electrochemical module temperature control loop. The pump uses 115V AC, 60 Hz power. Operation is automatic and continuous when system power is on, but can be manually overriden by a switch located on the back of the control instrumentation package.

8. Water Accumulator - The water accumulator feeds pure water to the electrochemical cell water feed cavities. The accumulator has two compartments separated by an ethylene propylene bladder. One compartment is connected to the module H_2 exhaust line and the other contains pure water. The bladder arrangement is used to equalize pressure between the cell's H_2 and water cavities, and prevent H_2 and water from mixing both in the accumulator and the cell cavities. The location of the water accumulator is shown in Figure 14.

9. Deionization Cartridge - The deionization cartridge purifies water feed to the system for use in the electrochemical cells. The cartridge serves primarily as a protective device against possible electrolyte contamination by ions in the inlet water.

10. Flow Restrictors - Five flow restrictors (orifices) are used in the system; three are used to distribute flow evenly to the three N_2 purge lines and two are used to slowly depressurize system components during mode transitions.

11. Check Valves - Three check valves are used on the N_2 purge feed lines to prevent gases from mixing through the purge lines.

12. Pressure Sensors - The two pressure sensors are used in the system. One, a transducer, is used to monitor electrochemical H_2 cavity pressure and contains built-in conditioning electronics. The second is a pressure switch and is used to signal the WATER FILL mode to end.

13. Differential Pressure Sensor - The differential pressure sensor is used to monitor electrochemical N_2-to-H_2 differential pressure. The transducer contains built-in conditioning electronics.

14. Temperature Sensors - Four temperature sensors are used to monitor inlet gas, electrochemical module, coolant and control electronics temperature. The inlet gas, module, and coolant temperature sensors consist of 1/8" diameter stainless steel probes which are inserted into the system fluid lines. Inside of these 1/8" diameter probes is a thermistor which is located at the very tip of the probe. The control electronics temperature sensor is a small aluminum disk to which a thermistor is bonded. The disk is in turn bonded to a heat sink in the control instrumentation.

15. Flow Sensor - The flow sensor consists of two separate, electrically heated, glass enclosed thermistors. Each thermistor is inserted into a hole in a small metal disk and bonded to the disk by a glass-to-metal seal. The metal disk is in turn soldered into a stainless steel tube. One thermistor assembly is inserted into the N_2 product gas line and the other is placed near but not in the direct gas stream.

16. Control Instrumentation - The front panel of the control instrumentation package (Figure 15) contains the mode indicators, the manual input pushbuttons, and an operating time readout. The rear of the control instrumentation (Figure 16) provides access to the connectors used for interconnection with the monitor instrumentation, power input, and GSA and the power input circuit breakers. The manual adjustments for temperature and Stage 2 current, the automatic manual switch for Stage 2 current, and the override switches are located on the back panel. Access to the 10 PC cards in the control instrumentation is from the back of the package. Table 6 lists the 10 cards included in this system by name, function, location, card number,, and LSI drawing number.

17. Monitor Instrumentation - The front panel of the monitor instrumentation package (Figure 17) is the Performance Trend and Fault Analysis Panel and contains the green, amber, flashing red, and red indicators for the eight parameters monitored, the cell counter display, and the lamp test and monitor reset pushbuttons. The rear of the monitoring instrumentation (Figure 18) contains the connectors used for interconnection with the control instrumentation, power input and GSA, and the power circuit breakers for the monitoring system. The override switches which allow the shutdown signal from any of the monitor circuit cards to be disconnected from the shutdown bus are located on the back panel. These switches are provided for troubleshooting or special system testing purposes. For normal operation, each of these switches would be in the closed position, which connects the PC card shutdown signal output to the shutdown bus. Access to the 11 monitoring PC cards is from the rear of the package. These cards are listed in Table 7 by name, function, location, card number, and LSI drawing number.

GROUND SUPPORT ACCESSORIES

The GSA were required to test the Polymer-Electrochemical N_2/H_2 Separator System. The functions of the GSA were to simulate fluid interfaces, supply power to the system and monitor and display performance data for the system. A photograph of the entire test facility showing the Polymer-Electrochemical N_2/H_2 Separator System and GSA is presented in Figure 19.

Fluid Interface Simulation

The GSA performs three fluid interface simulation functions:

1. Supplies process fluids to the system.

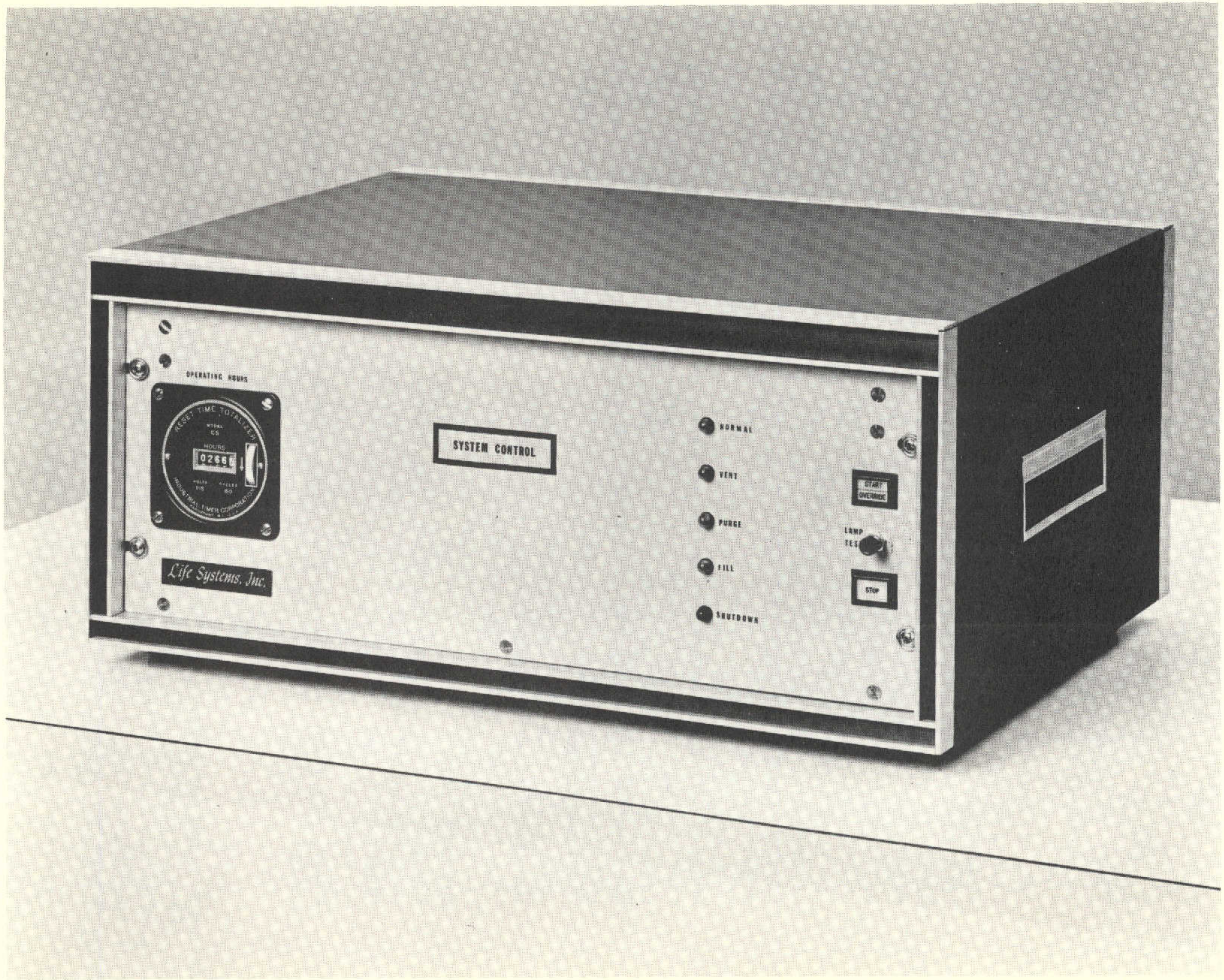

FIGURE 15 CONTROL INSTRUMENTATION PACKAGE SHOWING SYSTEM CONTROL PANEL

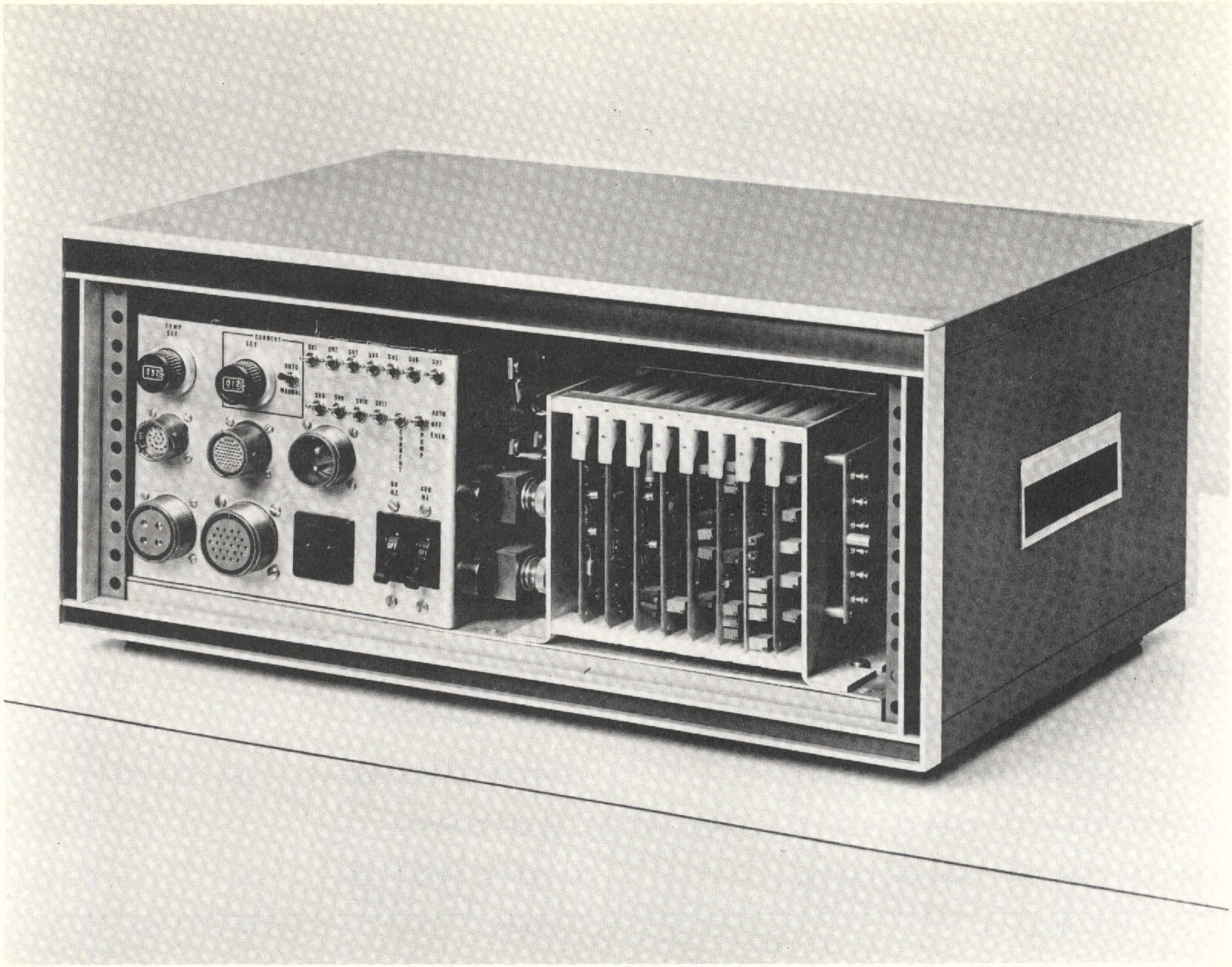

FIGURE 16 CONTROL INSTRUMENTATION PACKAGE (REAR VIEW) SHOWING OVERRIDE CONTROLS

TABLE 6 CONTROL INSTRUMENTATION PRINTED CIRCUIT CARD LIST

LSI Card Part No.	Schematic Drawing No.	Card[a] Location	Name	Function
A7	LSI-D-710	A	Water Tank Sequencer	Controls water tank fill sequence
A9	LSI-D-712	C	Five-Hour Clock & File Initiate	Initiates water tank fill sequence
A10	LSI-D-718	F	PWM Current Control	Control logic for Stage 2 current
A11	LSI-D-744	H	Temperature Control	Module Temperature control logic
A12	LSI-D-785	B	Main Sequencer	Controls System Start/Stop Sequences
A13	LSI-D-791	E	PWM Voltage/Current Control	Control logic for Stage 3 voltage & current
A14	LSI-D-809	D	Vent Control, Shutdown Timer	Controls Vent Mode & Time Delay
B3	LSI-D-279	G	Gas Flow Monitor	Monitor N_2 gas flow
H1	LSI-D-807	(b)	Valve Drivers	Power amplifiers to drive valves
H1	LSI-D-807	(b)	Valve Drivers	Power amplifiers to drive valves

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(a) Location of plug-in PC card in card guide assembly.
(b) Not a plug-in PC card. Located on chassis.

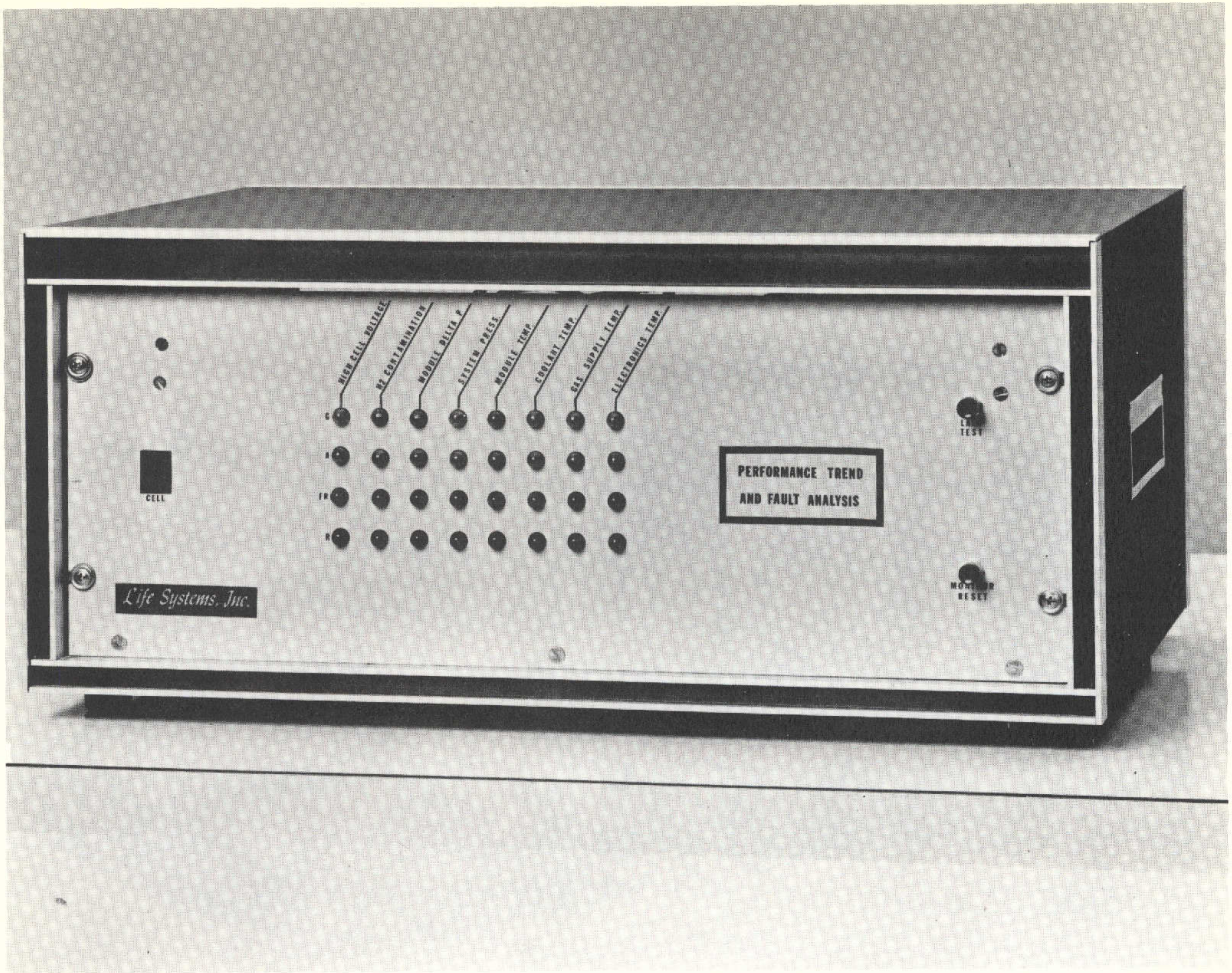

FIGURE 17 MONITOR INSTRUMENTATION PACKAGE SHOWING PERFORMANCE TREND AND FAULT ANALYSIS PANEL

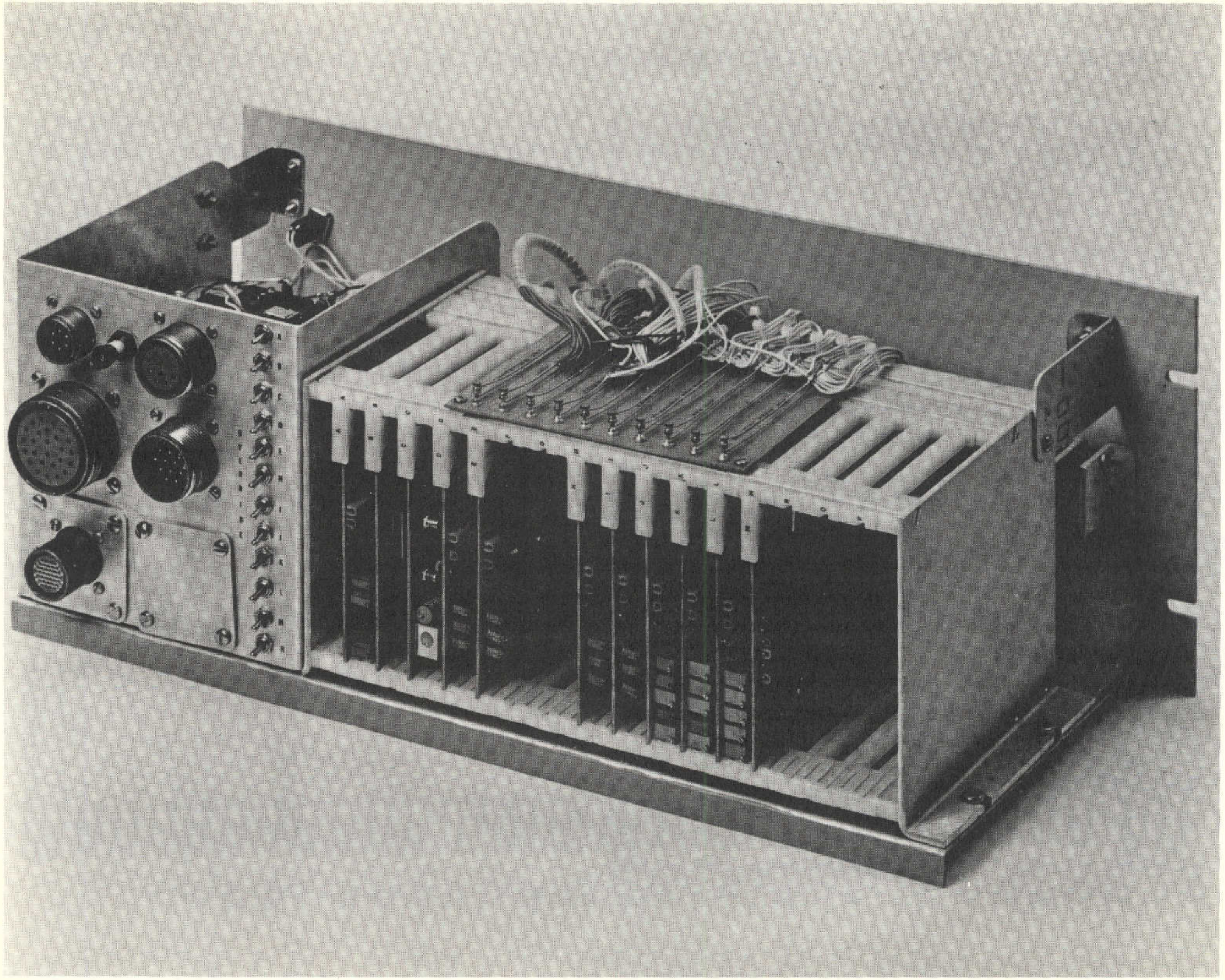

FIGURE 18 MONITOR INSTRUMENTATION PACKAGE (WITHOUT ENCLOSURE)

TABLE 7 MONITOR INSTRUMENTATION PRINTED CIRCUIT CARD LIST

LSI Card Part No.	Schematic Drawing No.	Card[a] Location	Name	Function
B2A-2I	LSI-D-278	L	Temperature Monitor	Monitor electronics temperature
B2A-2I	LSI-D-278	J	Temperature Monitor	Monitor coolant temperature
B2A-2I	LSI-D-278	K	Temperature Monitor	Monitor gas supply temperature
B6A-I	LSI-D-282	I	Transducer Output monitor	Monitor module temperature
B6A-I	LSI-D-282	E	Transducer Output Monitor	Monitor high module differential pressure
B6A-I	LSI-D-282	H	Transducer Output Monitor	Monitor high system pressure
B6A-I	LSI-D-282	D	Transducer Output Monitor	Monitor Stage 3 current (H_2 contamination)
B7-I	LSI-D-283	A	Voltage Level Monitor	Monitor high cell voltage
B9	LSI-D-285	C	Sensor Scan Control Logic	Operate scan relays on B10
B10	LSI-D-286	B	Scan Counter and Relays	Scan cells in module
B11	LSI-D-287	M	Status Indicator Logic	Flashing oscillator & status summary logic

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(a) Location of plug-in PC card in card guide assembly.

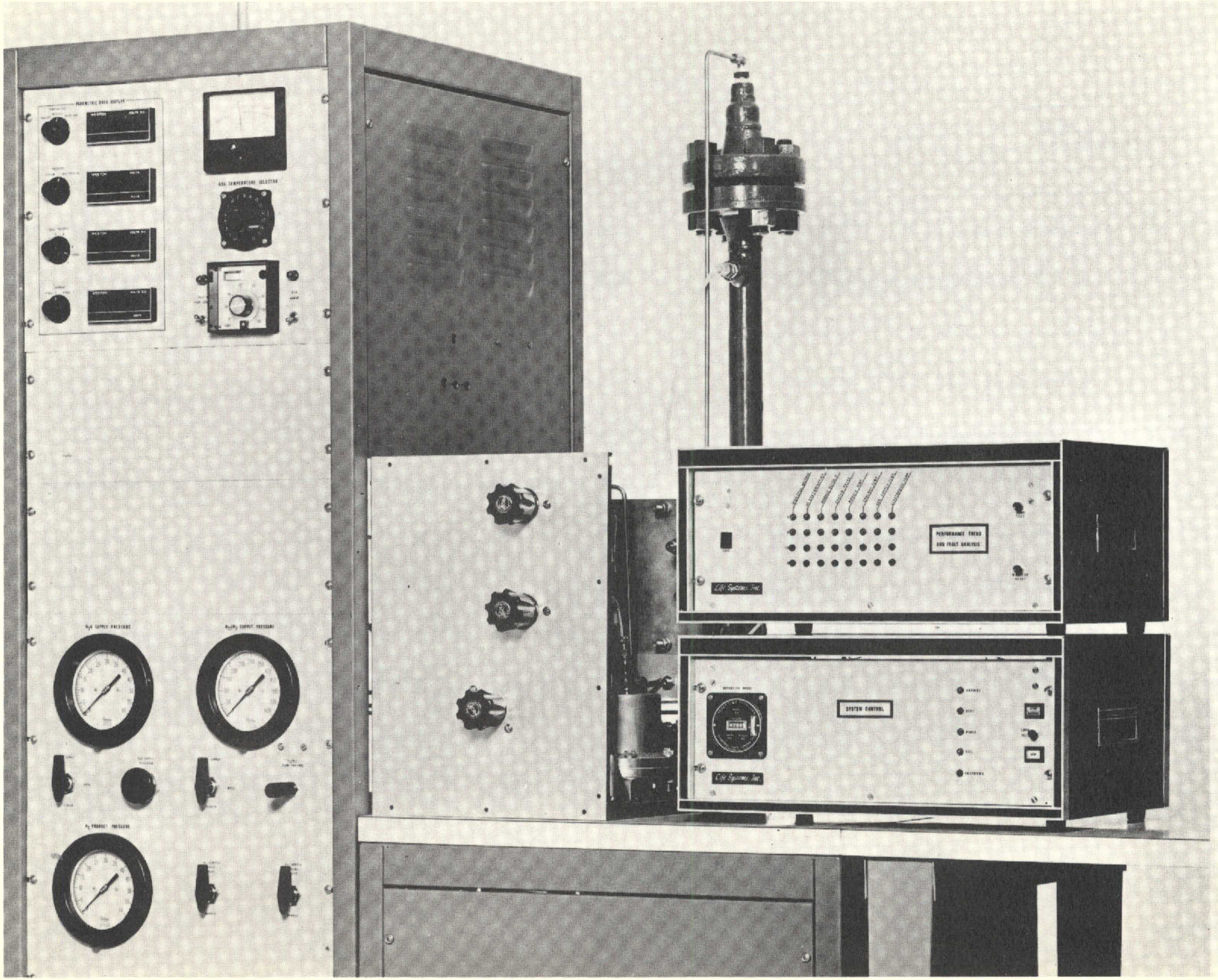


FIGURE 19 POLYMER-ELECTROCHEMICAL N_2/H_2 SEPARATOR TEST FACILITY

2. Provides for system venting and gas sampling.

3. Provides additional functions to aid in component and system testing.

The schematic for the fluid interface section of the GSA is given in Figure 20. A photograph of the fluid interface control panel section of the GSA is presented in Figure 21.

Fluid Supply Functions

Nitrogen/hydrogen gas mixture, process water for the electrochemical cells, coolant for system temperature control and purge N_2 are supplied to the system. Bottled, premixed N_2/H_2 gas is delivered to the Polymer-Electrochemical N_2/H_2 Separator System at the required pressure and flow rate. Tap water used by the electrochemical cells is regulated to 311 kN/m^2 (45 psia). Refrigerated coolant used in the system temperature control heat exchanger is supplied at 277K (40F). Bottled N_2 gas for use in purging the system during startup and shutdown is delivered to the system at 310 kN/m^2 (45 psia). A manual shutoff valve is provided for all fluid supply lines to the system.

Fluid Vent and Sampling Functions

The GSA provides for venting the product N_2 and H_2 gas streams. Impure product streams during system startup and shutdown are also vented through the same vent manifold provided by the GSA. Sampling valves on the product N_2 and H_2 vent lines are provided for product stream gas chromatographic analysis. Monitoring of the H_2 product pressure is provided since pressure monitoring was not provided nor required by the system for it to function.

Additional Functions

Two additional fluid interface functions are provided by the GSA; temperature control for the Polymer Diffusion Unit during checkout/characterization testing, and system component protection from damage caused by possible electrolyte entrainment in the product gas streams during system shakedown testing and electrochemical module checkout/characterization testing. Polymer Diffusion Unit temperature control is provided by circulating water at a controlled temperature through tubing wrapped around the outside of the polymer unit. Protection from electrolyte entrainment in the product gas streams is provided by a condenser, trap, and filter arrangement located on the H_2 and N_2 streams exhausting the electrochemical module. Both the polymer temperature control and the electrolyte traps on the product gas streams are not required during normal system operation.

Power Supply

The GSA supplies power to the system control instrumentation. The power required is supplied by a 10 A, 28 VDC power supply and a 115 VAC, 60 Hz power supply.

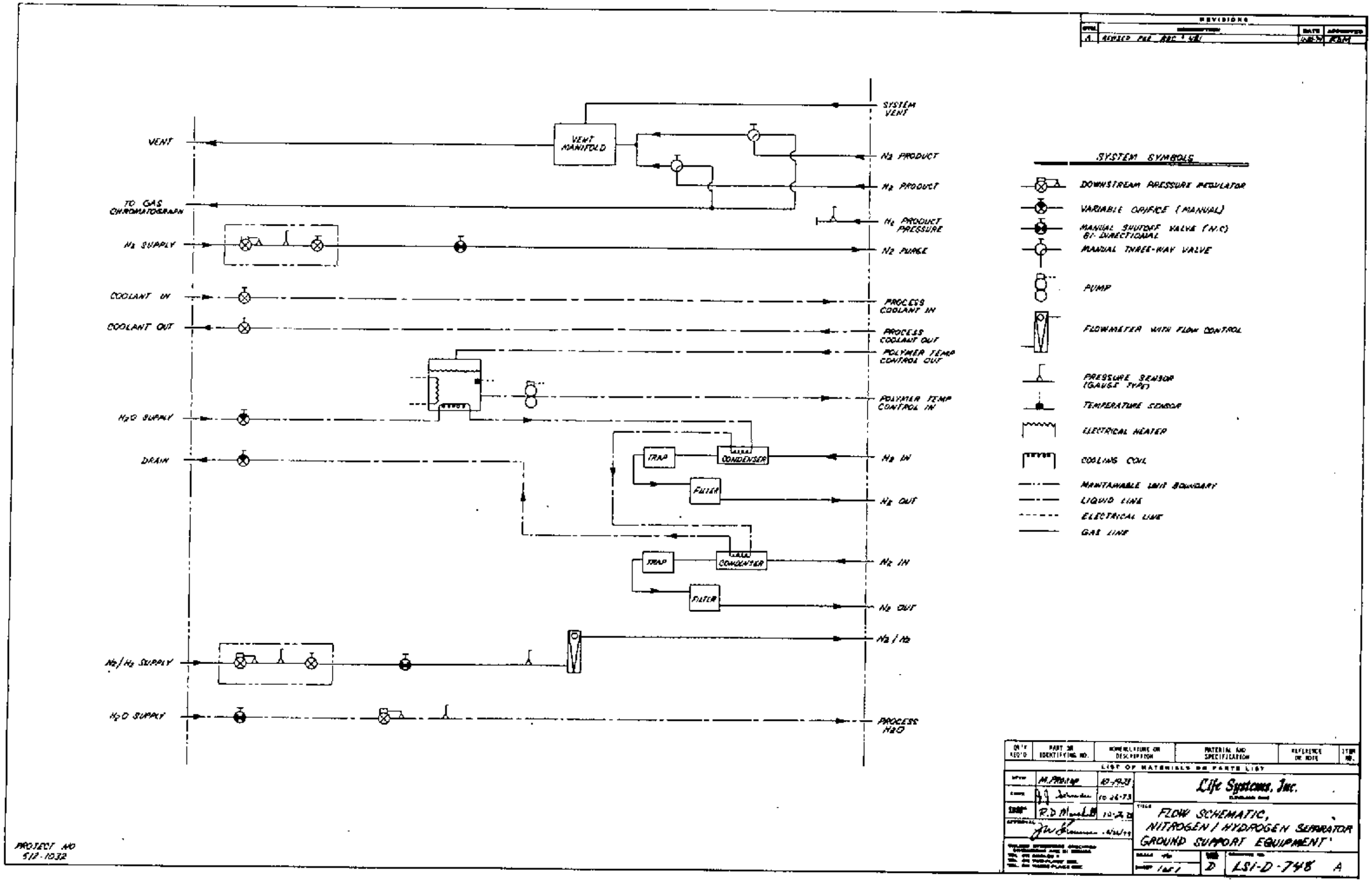


FIGURE 20 POLYMER-ELECTROCHEMICAL N_2/H_2 SEPARATOR GSA SCHEMATIC

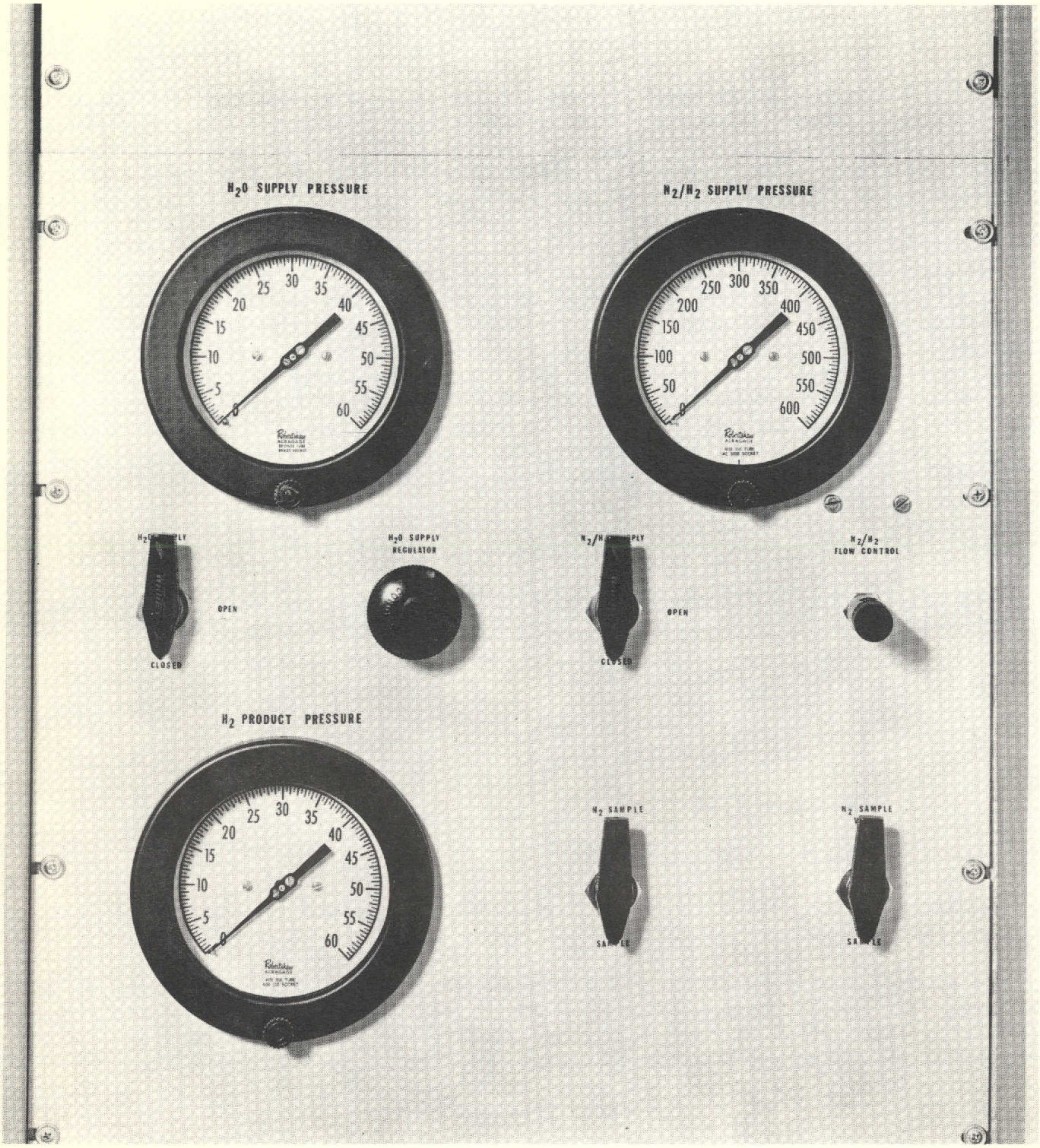


FIGURE 21 GSA FLUID INTERFACE PANEL

Parametric Data Display

The function of the parametric data display section of the GSA is to display system performance parameter levels and operating parameter data in engineering units. The parametric data display consists of four digital display units for 18 parameters. The parameters monitored are divided into four data groups; temperature, pressure, voltage, and current. The temperatures monitored are system inlet gas temperature, electrochemical module coolant temperature, and electrochemical module (H_2 out) temperature. The pressures monitored are electrochemcial module H_2 pressure, N_2 product pressure, and N_2-to-H_2 differential pressure. The nine individual cell voltages for the electrochemical module plus the second stage total voltage are read on the voltage display output. Electrochemical second and third stage currents are read on the current display output. In addition, a 16 position thermocouple switch and pyrometer are available for monitoring other temperatures as required during system testing. A photograph of the GSA electrical interface panel containing the parametric data display is presented in Figure 22. Located with parametric display on the panel are the polymer temperature controller, and the polymer liquid circulating pump power and total GSA power switches.

TEST PROGRAM

The Polymer-Electrochemical N_2/H_2 Separator Test Program consisted of three phases:

1. Component Checkout Tests
    a. Polymer Diffusion Unit
    b. Electrochemical Module
2. Shakedown Test
3. Design Verification Test

In addition, all other components were tested to insure they met specifications and all sensors were calibrated.

Integrated operation of the Polymer Diffusion Unit and Electrochemical N_2/H_2 Separator had not been previously demonstrated. Tests were run on the system to verify integration of the polymer and electrochemical N_2/H_2 Separators, and to establish system performance characteristics at the design point.

Component Checkout Tests

The Polymer Diffusion Unit and the Electrochemical N_2/H_2 Separator were tested individually to determine their performance characteristics prior to system integration.

Polymer Diffusion Unit Checkout Test

The Polymer Diffusion Unit checkout test consisted of monitoring the percentage of the feed H_2 removed as a function of N_2 delivery rate for 294K (70F) and 322K

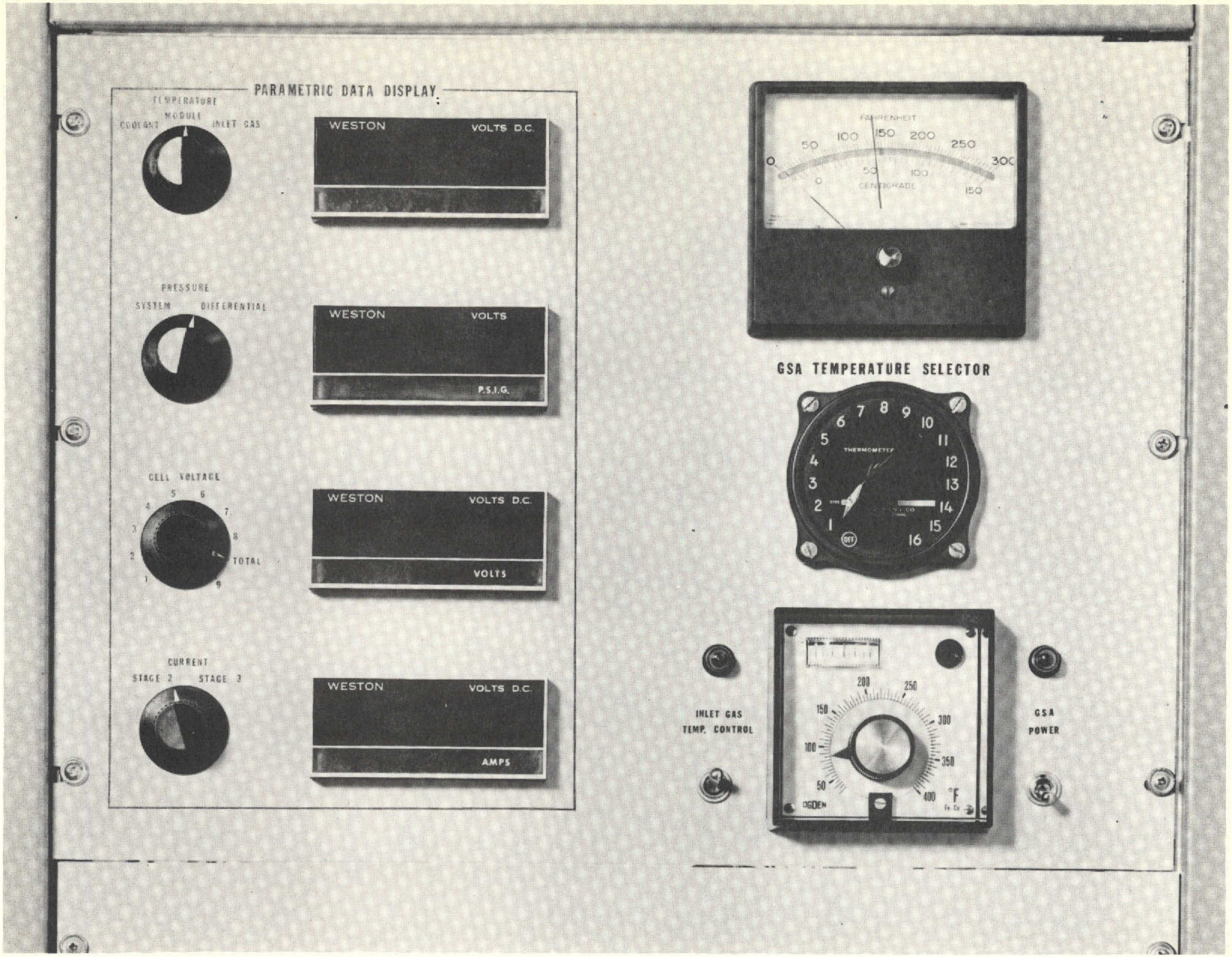


FIGURE 22 GSA ELECTRICAL INTERFACE PANEL

(120F). The N_2 product and H_2 product pressures for the test were 1035 kN/m^2 (150 psia) and 172 kN/m^2 (25 psia) respectively.

The results of the test are presented in Figure 23. The H_2 recovery percentage decreases linearly with increasing N_2 delivery rates for 1.5-6.8 kg/d (3.3-15.0 lb/day) at 294K (70F) and 2.7-6.8 kg/d (5.9-15.0 lb/day) at 322K (120F). Hydrogen recovery increases with increasing temperature. At the design point of 6.81 kg/d (15.0 lb/day) of N_2, the H_2 recovery was only 78% as compared to the desired 80-85% at 322K (120F). Although the performance of the unit was slightly less than expected, the performance was adequate to demonstrate integration with the Polymer-Electrochemical N_2/H_2 Separator. The electrochemical module would therefore have to remove slightly more H_2 than expected, but well within its capabilities (design point ±20%).

Electrochemical Module Checkout Test

A four-cell Electrochemical N_2/H_2 Separator module was tested to determine cell voltage as a function of current density prior to assembling the actual nine-cell module. The results of the current density span are presented in Figure 24. The average cell voltage was 0.06V at 108 mA/cm^2 (100 ASF) as compared to the expected voltage of 0.10V at 108 mA/cm^2 (100 ASF).

Shakedown Test

Following checkout tests and assembly of all components into the system, and system integration with the GSA, a Shakedown Test was performed. The Shakedown Test consisted of:

1. Verifying valve sequencing during mode transitions.
2. Verifying PC card set points for amber, flashing red, and red conditions.
3. Inducing shutdowns for each parameter monitored.
4. Timing the pressure decay and electrochemical module differential pressure after inducing a shutdown.
5. Checking for leaks.
6. Insuring all manual controls and overrides were operable.
7. Establishing the automatic current/voltage control set points.

The shakedown testing consumed 60 hours of integrated system and GSA operation, and resulted in the following modifications:

1. During the testing the epoxy seal in the Polymer Diffusion Unit failed and resulted in replacement of the unit.

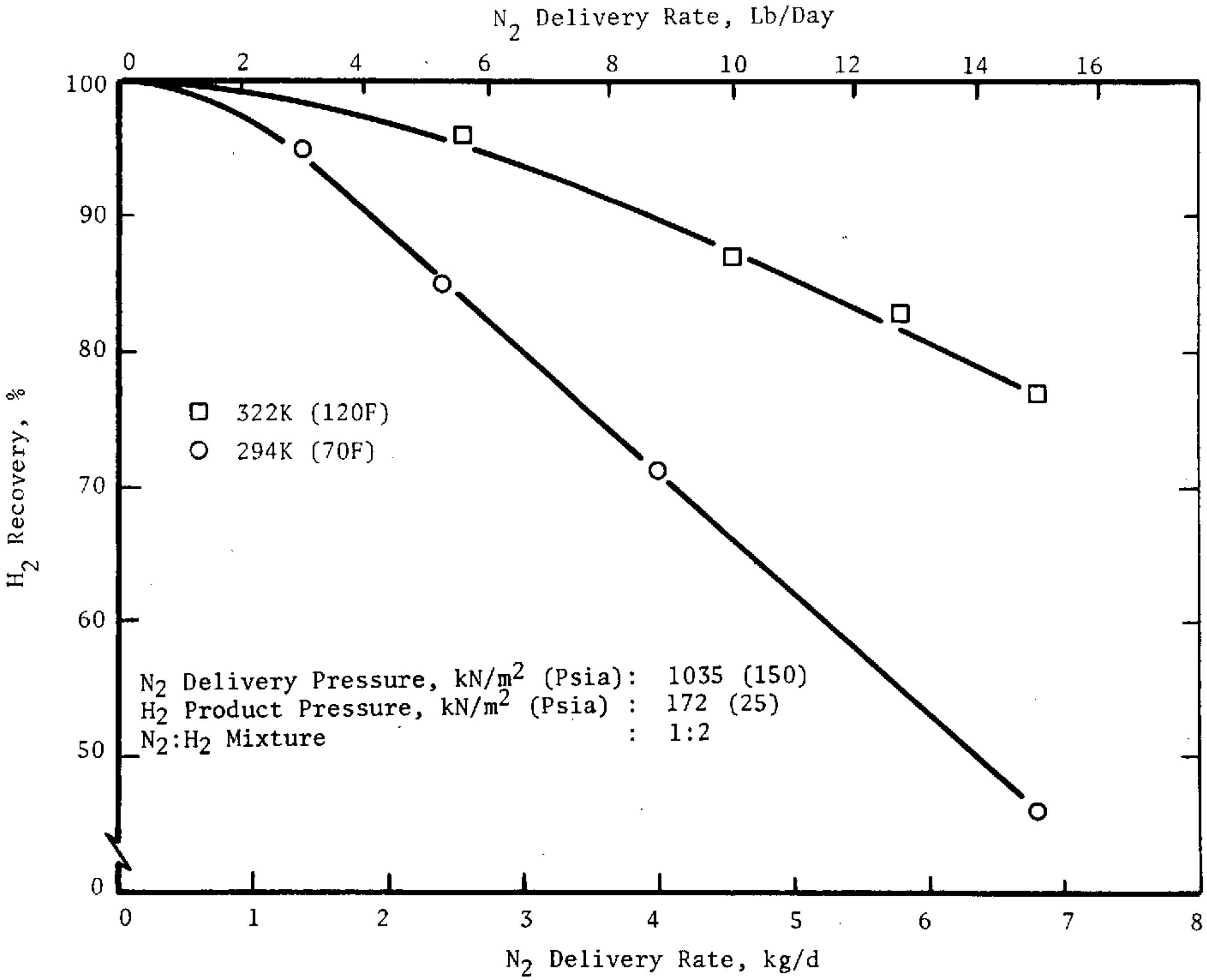


FIGURE 23 EFFECT OF N_2 DELIVERY RATE AND TEMPERATURE ON POLYMER N_2/H_2 SEPARATOR PERFORMANCE

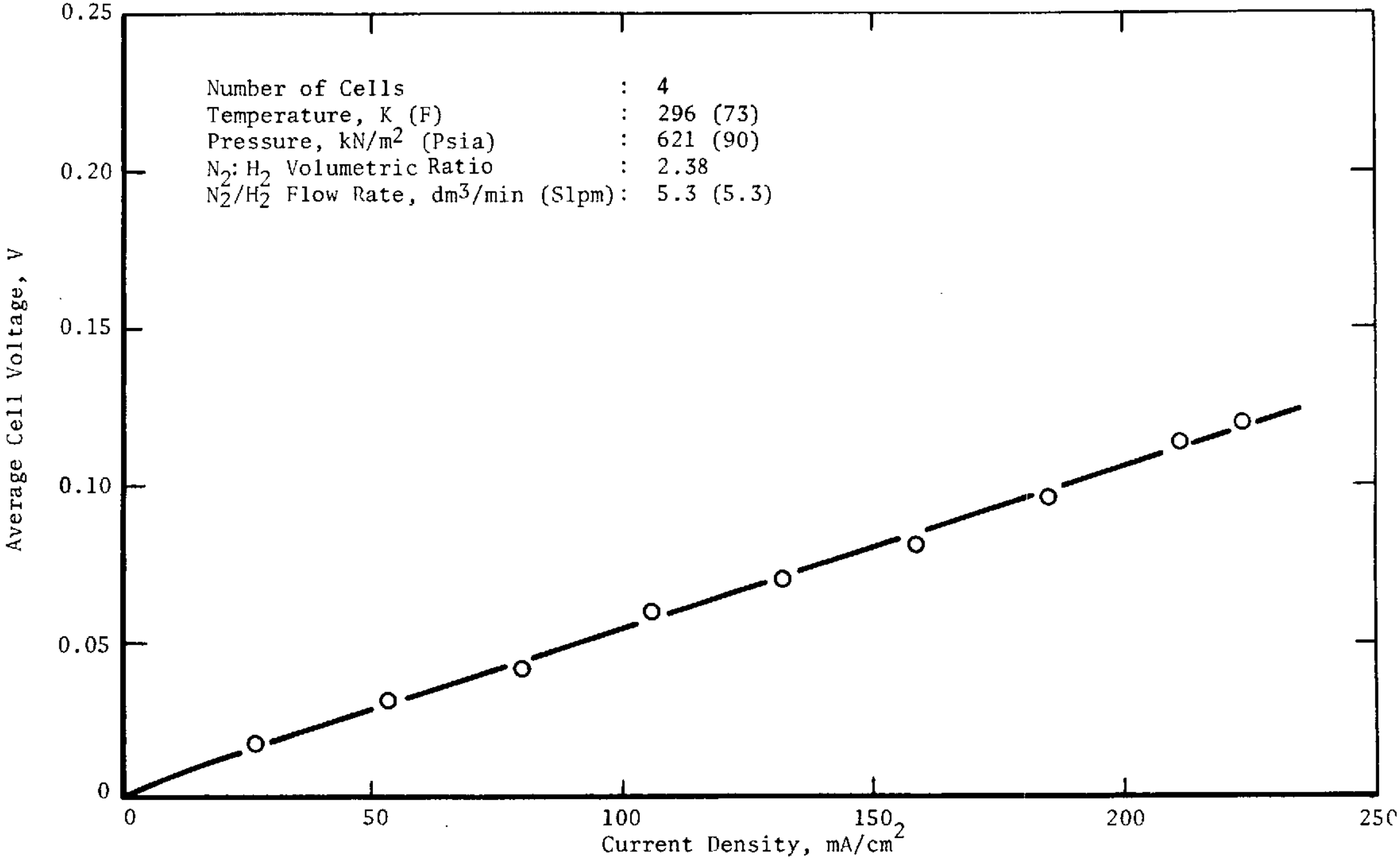


FIGURE 24 EFFECT OF CURRENT DENSITY ON ELECTROCHEMICAL N_2/H_2 SEPARATOR PERFORMANCE

2. A check valve on the N_2 purge line to the electrochemical module failed and was replaced.

3. Pressure decay time for the system was too long and resulted in replacement of an orifice.

4. High electrochemical module differential pressures (27.6 kN/m^2 (4 psid)) were observed during startup and shutdown sequencing which resulted in a modification to the differential pressure regulator (DPR1).

5. The electrochemical Stage 2 to Stage 3 current ratio was set at 1:1 and the Stage 3 voltage limit was set at 0.51V.

Design Verification Test

A 200-hour DVT was run on the system to establish Polymer-Electrochemical N_2/H_2 Separator performance characteristics as a function of time. Performance is measured by the product gas purity, electrochemical module power required (i.e., cell voltage and current), and first stage H_2 recovery. The results of the DVT are presented in Figure 25. The operating conditions for the test are presented in Table 8.

The DVT was conducted for two moninal N_2 delivery rates; 5.3 kg/d (11.7 lb/day) for the first 50 hours and 6.8 kg/d (15.0 lb/day) for the last 150 hours. The system met or exceeded the design point for both N_2 delivery rates. The average N_2 and H_2 product gas purities were 99.8% and 98.3% by volume, respectively. The H_2 product gas purity, however, decreased to 97.5% at the lower N_2 delivery rate. The first stage H_2 recovery was approximatley 85% and showed a slight increase with N_2 delivery rate. This increase is attributed to the increase in the inlet feed gas pressure required to attain the higher flow rate (a pressure increase of approximately 207 kN/m^2 (30 psia)). The average electrochemical second stage voltage was 0.10V/cell at a current level of 19A or 85 mA/cm^2 (92 ASF). The average electrochemical cell power requirement was approximately 25W.

PALLADIUM/SILVER N_2/H_2 SEPARATOR

The function of the Pd/Ag N_2/H_2 Separator is to separate 6.81 kg/d (15 lb/day) of N_2 from 0.98 kg/d (2.14 lb/day) of H_2 and deliver the N_2 product gas at an elevated pressure for spacecraft N_2 resupply applications. The Pd/Ag N_2/H_2 Separator consists of two Pd/Ag Diffusion Units connected in series. Each unit represents a stage. The first stage recovers 80-85% of the feed H_2 at a useable pressure. The second stage removes the remaining H_2 to vacuum. Ground Support Accessories were developed to test the Pd/Ag N_2/H_2 separator and monitor its performance.

Palladium/Silver Diffusion Unit Design

A functional schematic of a Pd/Ag Diffusion Unit is given in Figure 26. The Pd/Ag tubes are suspended from a manifold plate into the diffusion unit housing. The tubes are sealed at one end. The N_2/H_2 gas mixture enters the shell side

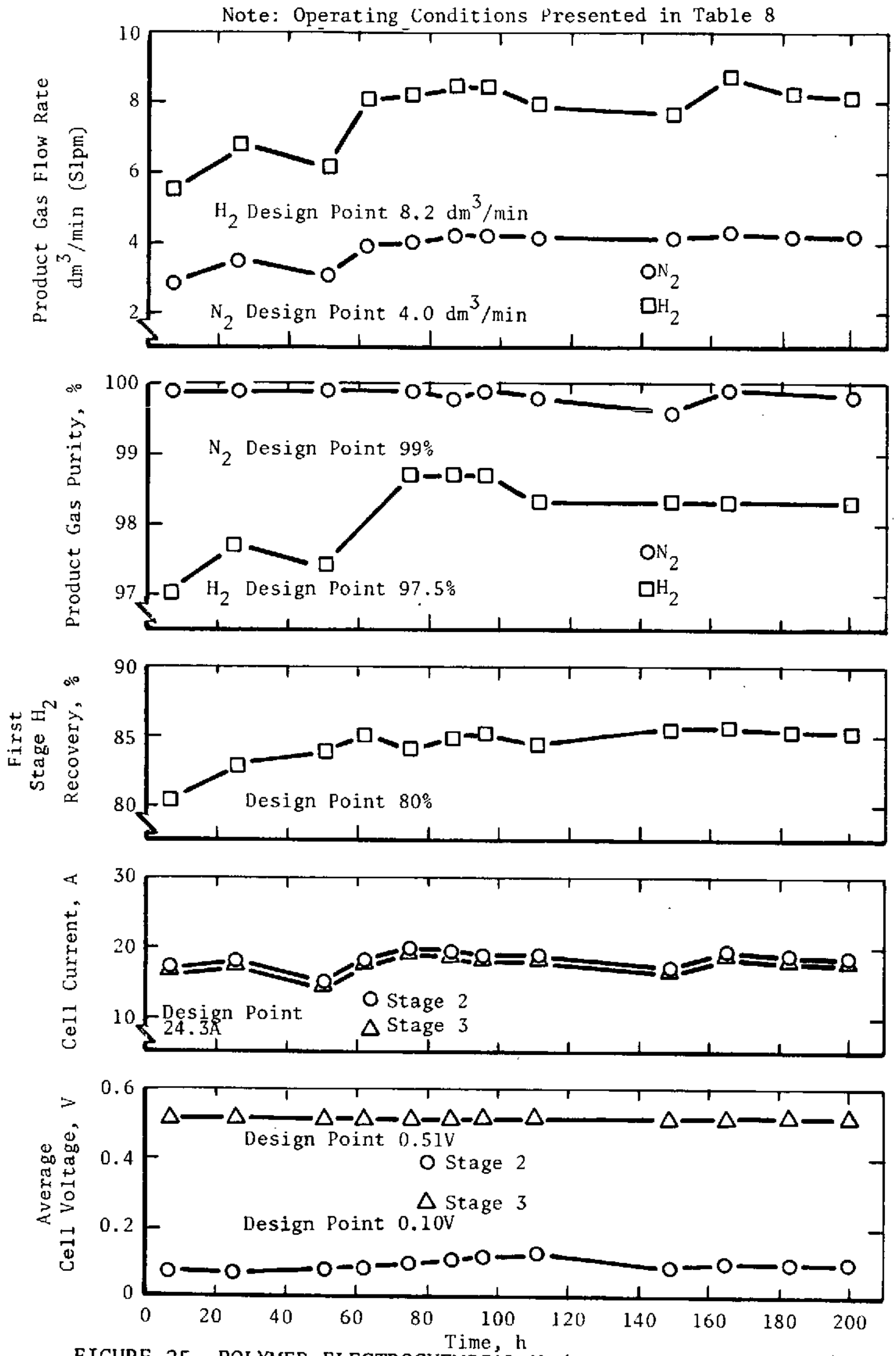


FIGURE 25 POLYMER-ELECTROCHEMICAL N_2/H_2 SEPARATOR DVT

TABLE 8 POLYMER-ELECTROCHEMICAL N_2/H_2 SEPARATOR OPERATING CONDITIONS

N_2/H_2 Feed	
Flow Rate,(a) kg/d (Lb/Day)	5.4 - 6.6 (11.9 - 14.5)
dm^3/min (Slpm)	8.5 - 10.3 (8.5 - 10.3)
Flow Rate,(b) kg/d (Lb/Day)	7.7 - 8.4 (17.0 - 18.5)
dm^3/min (Slpm)	12.1 - 12.5 (12.1 - 12.5)
Composition (by volume)	
N_2, %	33
H_2, %	67
Temperature, K (F)	294 - 298 (70 - 77)
N_2 Product	
Temperature, K (F)	294 - 298 (70 - 77)
Pressure, kN/m^2 (Psia)	1035 - 1042 (150 - 151)
H_2 Product	
Temperature, K (F)	294 - 298 (70 - 77)
Pressure, kN/m^2 (Psia)	173 - 179 (25 - 26)
Polymer Diffusion Unit	
Temperature, K (F)	297 - 298 (75 - 77)
Electrochemical Module	
Temperature, K (F)	297 - 300 (76 - 81)
Current Control Ratio, A/A	1.00 - 1.07
Control Voltage, V	0.51

(a) For first 50 hours.
(b) For last 150 hours.

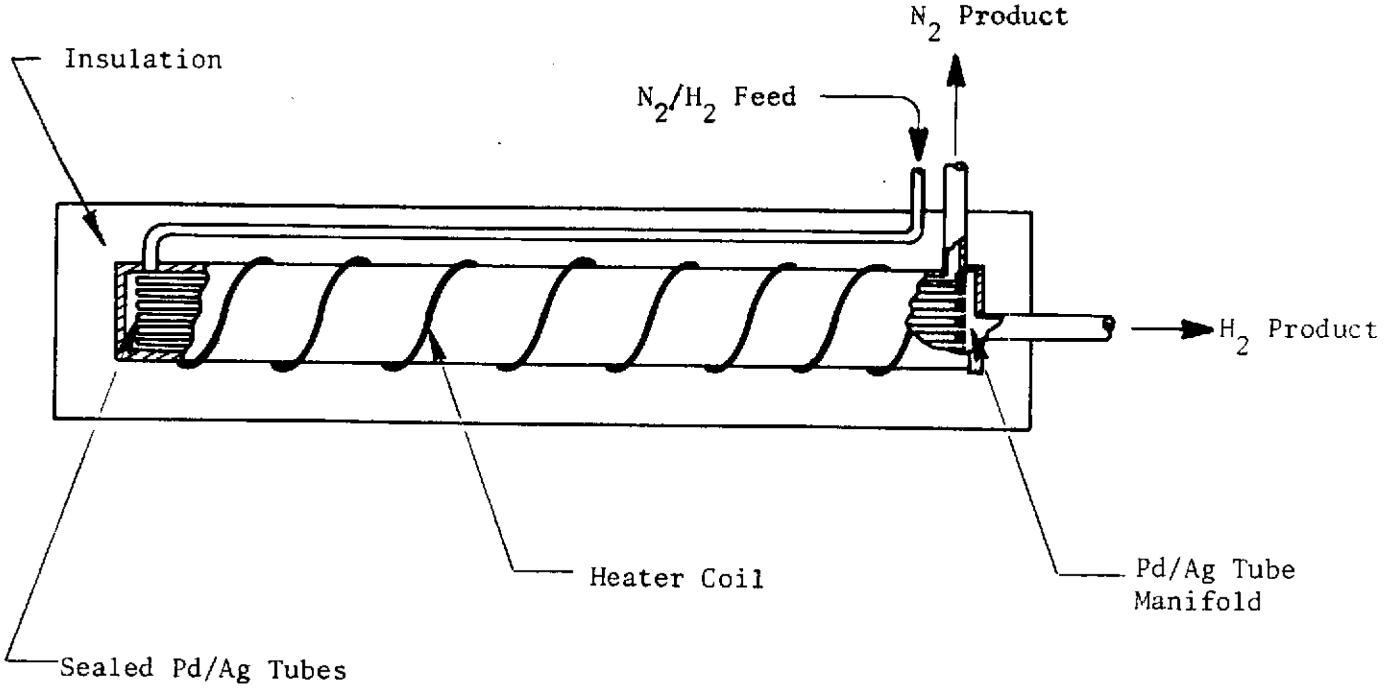


FIGURE 26 Pd/Ag DIFFUSION UNIT SCHEMATIC

traveling the length of the unit to preheat. Hydrogen diffuses into the Pd/Ag tubes and is manifolded from the Pd/Ag N_2/H_2 Separator. The H_2-depleted-N_2 product stream is manifolded from the shell side at the same end of the unit as the H_2 product. A photograph of a Pd/Ag Diffusion Unit is presented in Figure 27.

The design specifications for the Pd/Ag N_2/H_2 Separator are listed in Table 9. Two Pd/Ag Diffusion Units as described above are used for the two stages. The N_2/H_2 feed mixture enters the Pd/Ag Diffusion Unit in the shell side of the first stage at 1690 kN/m^2 (245 psia) and 644K (700F). Hydrogen diffuses into the tubes under a H_2 partial pressure (pH_2) driving force and exhausts through the tube manifold plate at 172 kN/m^2 (25 psia) for spacecraft usage. The H_2-depleted mixture from the shell side of the first stage enters the shell side of the second stage. The remaining H_2 diffuses into the tubes of the second stage and is vented to vacuum. The purified N_2 from the shell side of the second stage is available for spacecraft usage at approximately the same pressure as the N_2/H_2 feed.

Ground Support Accessories

The function of the GSA is to test the Pd/Ag N_2/H_2 Separator. The mechanical and electrical components required to control operation and monitor performance are located in a single package along with the two Pd/Ag Diffusion Units. A photograph of the test facility is presented in Figure 28.

Mechanical Design and Operation

Figure 29 is a schematic of the Pd/Ag GSA test facility. The N_2/H_2 gas mixture is supplied to the test facility. A gas flow controller maintains the flow rate to the Pd/Ag N_2/H_2 Separator. A solenoid valve (SV1) is provided to shut off the flow of N_2/H_2 feed during shutdown. Hydrogen is removed from the feed gas stream as it flows through the two successive H_2 removal stages. The temperature of the N_2 product gas is then reduced to ambient by a heat exchanger (HX2). The H_2 delivery pressure is controlled by a backpressure regulator (PR2) located downstream from HX2. The pressure of the gas stream before and after the Pd/Ag N_2/H_2 Separator is measured by gauges G1 and G4.

The H_2 removed in the first stage is cooled in a heat exchanger (HX1) and its pressure is controlled by a backpressure regulator (PR1). The H_2 is removed in the second stage to vacuum using a vacuum pump. No heat exchanger was required to cool the second stage H_2 because of the low mass and high volumetric H_2 flow rate in the vacuum line. The H_2 pressure for each stage is measured by gauges G2 and G3.

Nitrogen purge is provided manually for the first stage H_2 lines and components, and automatically for the second stage H_2 lines and components. Valves V1 and V2 are used for the manual purge operation. Solenoid valves SV2 and SV3 are used to automatically purge the vacuum lines following a shutdown to prevent ambient air from leaking into the evacuated lines.

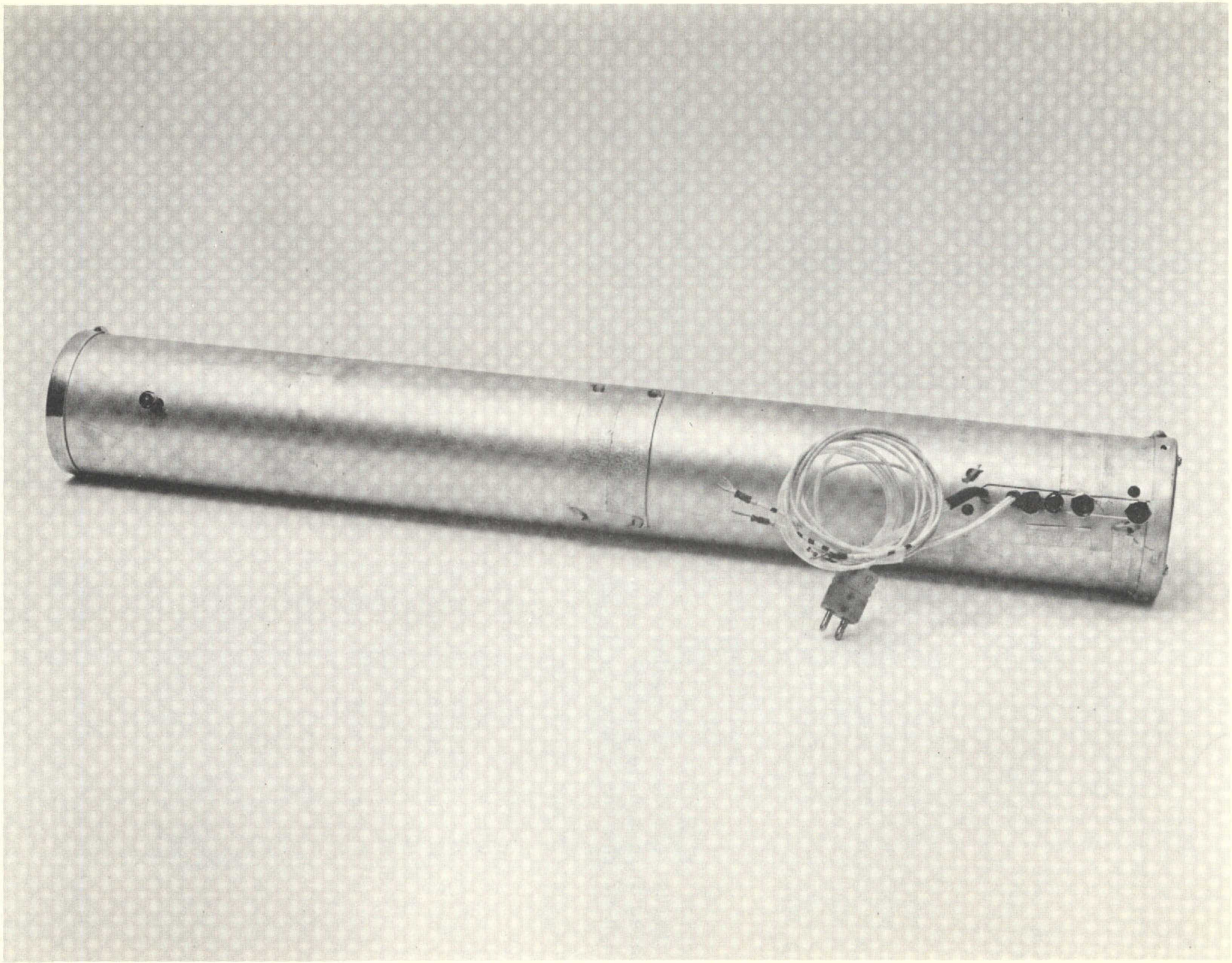


FIGURE 27 PALLADIUM/SILVER DIFFUSION UNIT

TABLE 9 PALLADIUM/SILVER N_2/H_2 SEPARATOR DESIGN SPECIFICATIONS

N_2/H_2 Feed	
Source	Premixed N_2/H_2
Flow Rate	
Nominal, kg/d (Lb/Day)	7.78 (17.14)
dm^3/min (Slpm)	12.2 (12.2)
Minimum, kg/d (Lb/Day)	3.6 (8.0)
dm^3/min (Slpm)	5.7 (5.7)
Maximum, kg/d (Lb/Day)	8.2 (18.0)
dm^3/min (Slpm)	12.8 (12.8)
Composition (by volume)	
N_2, %	33
H_2, %	67
Temperature, K (F)	293 - 700 (68 - 800)
Pressure	
Nominal, kN/m^2 (Psia)	1690 (245)
Minimum, kN/m^2 (Psia)	1552 (225)
Maximum, kN/m^2 (Psia)	2070 (300)
N_2 Product	
Flow Rate	
Nominal, kg/d (Lb/Day)	6.8 (15.0)
dm^3/min (Slpm)	4.0 (4.0)
Minimum, kg/d (Lb/Day)	3.2 (7.0)
dm^3/min (Slpm)	1.9 (1.9)
Maximum, kg/d (Lb/Day)	6.8 (15.0)
dm^3/min (Slpm)	4.0 (4.0)
Purity (by volume)	
Minimum, %	99.0
Maximum, %	99.9+
Temperature, K (F)	293 - 298 (68 - 77)
Pressure	
Nominal, kN/m^2 (Psia)	1649 (244)
Minimum, kN/m^2 (Psia)	1546 (224)
Maximum, kN/m^2 (Psia)	2063 (299)

continued-

Table 9 - continued

H_2 Product	
Flow Rate	
Nominal, kg/d (Lb/Day)	0.78 (1.71)
dm^3/min (Slpm)	6.5 (6.5)
Minimum, kg/d (Lb/Day)	0.45 (1.0)
dm^3/min (Slpm)	3.8 (3.8)
Maximum, kg/d (Lb/Day)	0.81 (1.78)
dm^3/min (Slpm)	6.8 (6.8)
Purity (by volume), %	99.9999 - 100
Temperature, K (F)	293 - 298 (68 - 77)
Pressure	
Nominal, kN/m^2 (Psia)	172 (25)
Minimum, kN/m^2 (Psia)	104 (15)
Maximum, kN/m^2 (Psia)	310 (45)
H_2 Vented	
Flow Rate	
Nominal, kg/d (Lb/Day)	0.19 (0.43)
dm^3/min (Slpm)	1.63 (1.63)
Minimum, kg/d (Lb/Day)	0.10 (0.22)
dm^3/min (Slpm)	0.82 (0.82)
Maximum, kg/d (Lb/Day)	0.20 (0.45)
dm^3/min (Slpm)	1.71 (1.71)
Temperature, K (F)	293 - 298 (68 - 77)
Pressure	
Nominal, kN/m^2 (mm Hg)	0.67 (5)
Minimum, kN/m^2 (mm Hg)	0 (0)
Maximum, kN/m^2 (mm Hg)	1.33 (10)
Electrical Power	
Supply Voltage, VAC	115±10 and 230±20
Hz	60
Power Supply	
Type Gas	N_2
Pressure, kN/m^2 (Psia)	310 (45)
Coolant Supply	
Type	Air
Temperature, K (F)	293 - 298 (68 - 77)

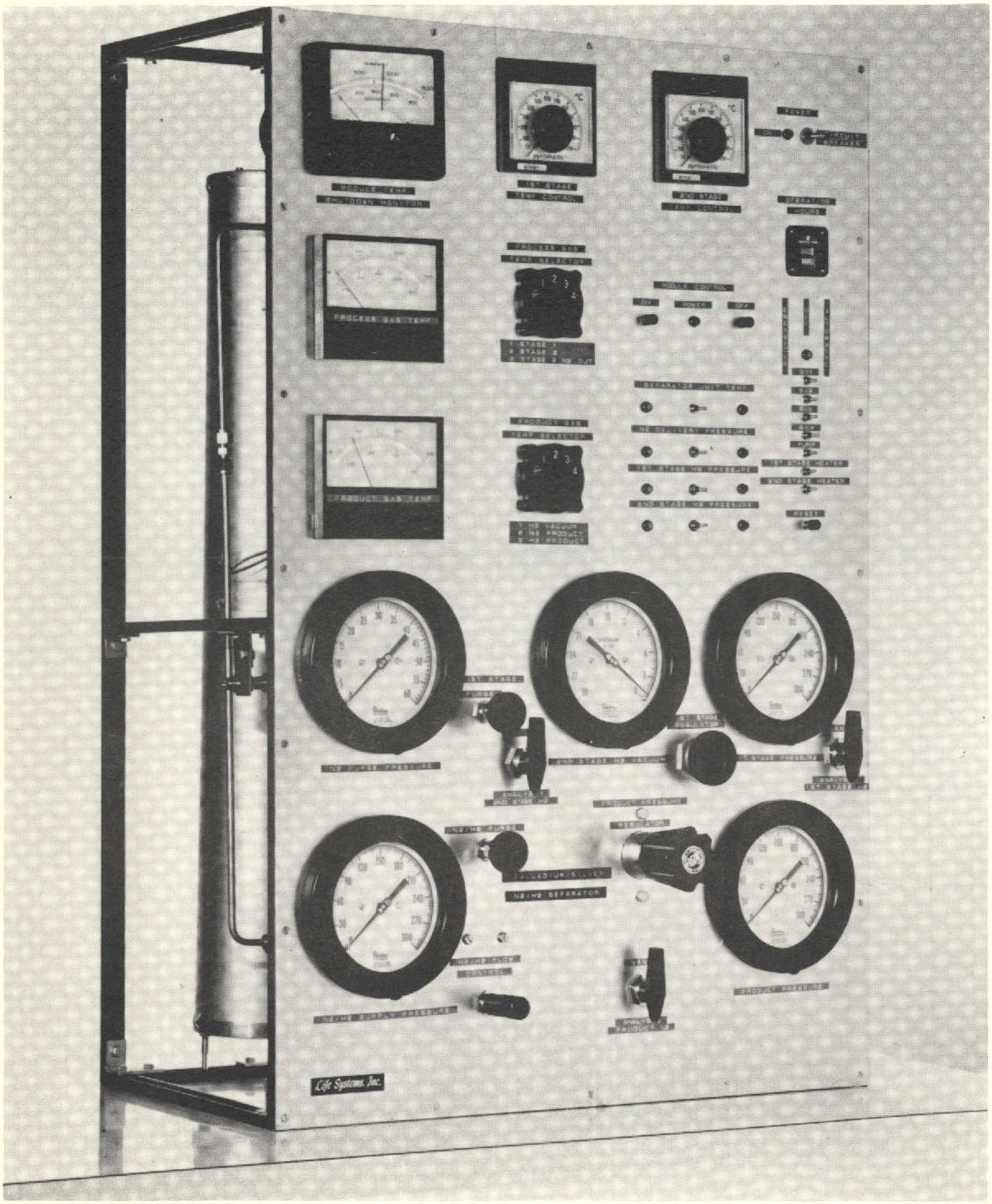
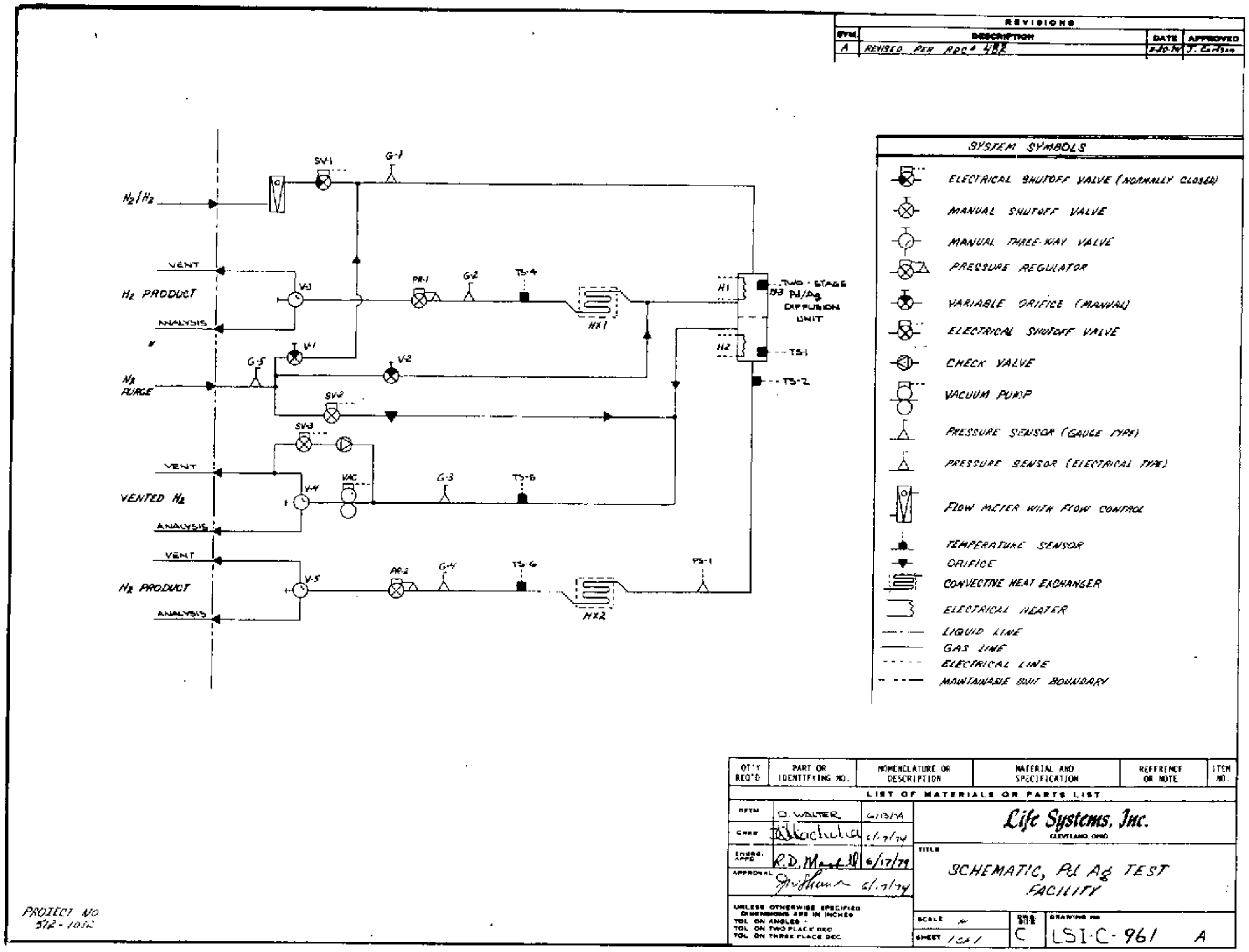


FIGURE 28 PALLADIUM/SILVER TEST FACILITY



REVISIONS			
SYM.	DESCRIPTION	DATE	APPROVED
A	REVISED PER RRC# 482	8-20-74	J. Carlson

QT'Y REQ'D	PART OR IDENTIFYING NO.	NOMENCLATURE OR DESCRIPTION	MATERIAL AND SPECIFICATION	REFERENCE OR NOTE	ITEM NO.

LIST OF MATERIALS OR PARTS LIST

DFTM D. WALTER 6/13/74
CHKD 6/17/74
ENGRG. APPD R.D. 6/17/74
APPROVAL 6/17/74

Life Systems, Inc.
CLEVELAND, OHIO

TITLE SCHEMATIC, Pd Ag TEST FACILITY

UNLESS OTHERWISE SPECIFIED
DIMENSIONS ARE IN INCHES
TOL ON ANGLES ±
TOL ON TWO PLACE DEC
TOL ON THREE PLACE DEC

SCALE —
SHEET 1 of 1
DWG SIZE C
DRAWING NO. LSI-C-961 A

FIGURE 29 Pd/Ag TEST FACILITY SCHEMATIC

Instrumentation Design

Instrumentation is provided to:

1. Control the temperature of the diffusion units.
2. Monitor system temperatures.
3. Control solenoid valve operation.
4. Provide automatic shutdown for excessive diffusion unit temperature and pressure.

Diffusion unit temperature control is provided by a separate temperature controller for each stage. Temperature monitoring is provided by six thermocouples connected to pyrometers located on the front panel. Solenoid valves operation is controlled by energizing the solenoids during normal running and deenergizing during shutdown. Temperature shutdown is signaled by thermocouple TS1. Pressure shutdown is signalled by pressure switch (PS1).

The electrical power sources required to operate the instrumentation are 115VAC, 60 Hz power, which is converted to 24 VDC within the test stand to run the instrumentation, and 230 VAC, 60 Hz power for the diffusion unit heaters.

Test Program

The Pd/Ag N_2/H_2 Separator Test Program consisted of a Shakedown Test and a 200-hour DVT. In addition checkout testing was completed on all test facility components, and all parameter monitoring and control components were calibrated.

Shakedown Test

Following the assembly of the Pd/Ag N_2/H_2 Separator and the test facility, a Shakedown Test was performed to verify integrated Pd/Ag N_2/H_2 Separator and test facility operation. No modifications to the test facility or Pd/Ag N_2/H_2 Separator were required as a result of the Shakedown Test.

Design Verification Test

A 200-hour DVT was completed on the two-stage Pd/Ag N_2/H_2 Separator to establish its performance characteristics as a function of time. The Pd/Ag N_2/H_2 Separator performance is measured by N_2 product gas purity and first stage H_2 recovery.

The results of the DVT are presented in Figure 30. The operating conditions for the test are listed in Table 10. The N_2 product gas purity was 99.1%-99.9%. Purity was calculated by both volumetric and gas chromatographic techniques. The average first stage H_2 recovery was 85% of the H_2 in the feed gas mixture.

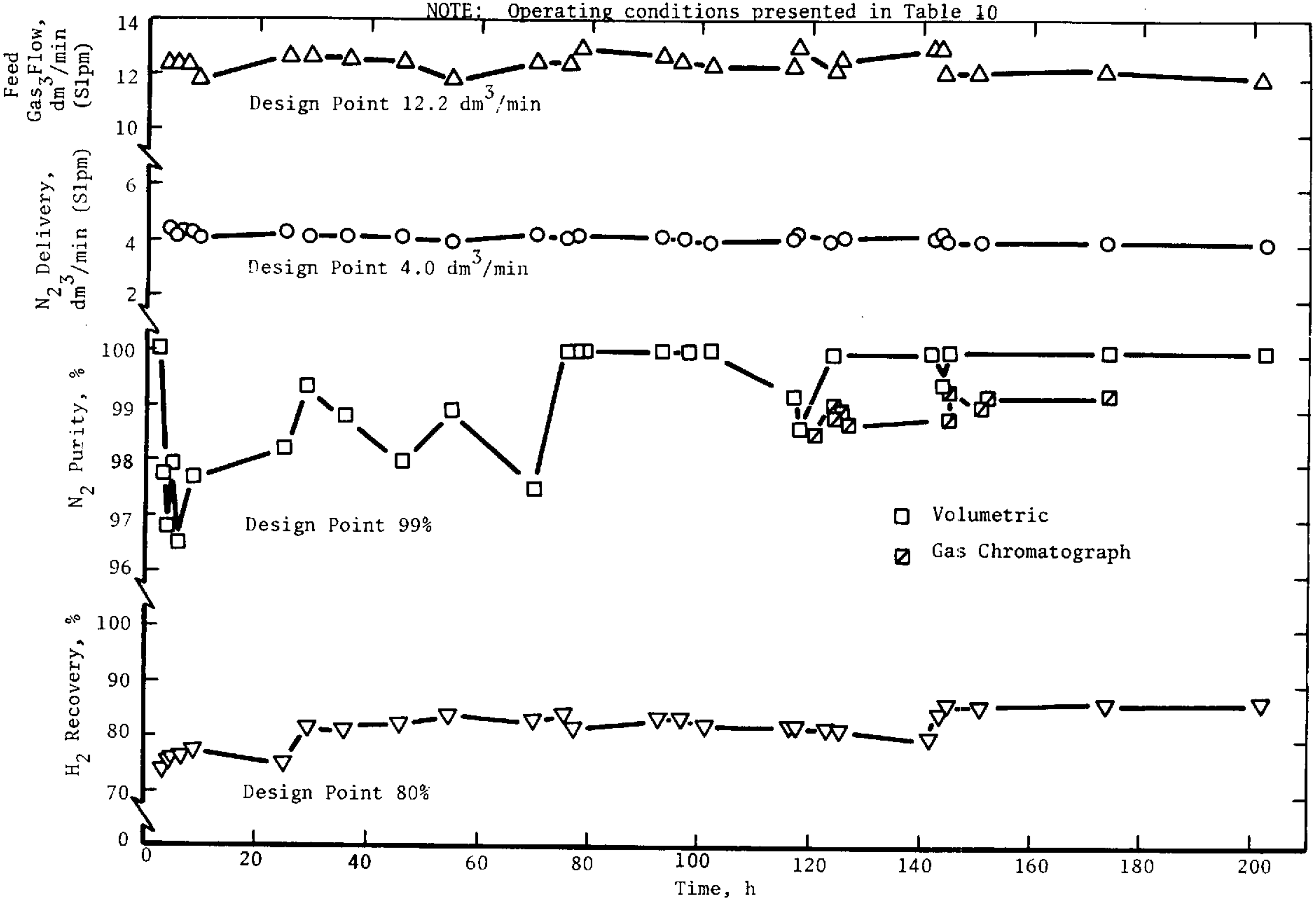


FIGURE 30 Pd/Ag N_2/H_2 SEPARATOR DVT

TABLE 10 Pd/Ag N_2/H_2 SEPARATOR OPERATING CONDITIONS

N_2/H_2 Feed	
Flow Rate, kg/d (Lb/Day)	7.7 - 8.4 (17.0 - 18.5)
dm^3/min (Slpm)	12.1 - 12.5 (12.1 - 12.5)
Composition (by volume)	
N_2, %	33
H_3, %	67
Temperature, K (F)	294 - 298 (70 - 77)
N_2 Product	
Temperature, K (F)	294 - 298 (70 - 77)
Pressure, kN/m^2 (Psia)	1656 - 1691 (240 - 245)
H_2 Product	
Flow Rate, kg/d (Lb/Day)	0.77 - 0.86 (1.7 - 1.9)
dm^3/min (Slpm)	6.5 - 7.1 (6.5 - 7.1)
Purity (by volume), %	100
Temperature, K (F)	294 - 298 (70 - 77)
Pressure, kN/m^2 (Psia)	173 - 179 (25 - 26)
H_2 Vent to Vacuum	
Flow Rate, kg/d (Lb/Day)	0.12 - 0.19 (0.26 - 0.42)
dm^3/min (Slpm)	1.0 - 1.6 (1.0 - 1.6)
Temperature, K (F)	294 - 298 (70 - 77)
Pressure, kN/m^2 (mm Hg)	0.53 - 0.80 (4 - 6)
Pd/Ag Diffusion Unit	
Temperature, K (F)	633 - 655 (680 - 720)

HYDRAZINE CATALYTIC DISSOCIATOR

The function of the N_2H_4 Catalytic Dissociator is to dissociate 7.78 kg/d (17.14 lb/day) of liquid N_2H_4 into an N_2/H_2 gas mixture and deliver the product gas at an elevated pressure for subsequent separation. The system consists of the N_2H_4 Catalytic Dissociator and the mechanical and electrical components required for system operation.

Dissociator Design

The N_2H_4 Catalytic Dissociator performs the actual N_2H_4 dissociation process. A schematic of the N_2H_4 Catalytic Dissociator is presented in Figure 31. Photographs of the assembled and disassembled N_2H_4 Catalytic Dissociator are presented in Figures 32 and 33, respectively.

Dissociator Operation

The reactor is heated to approximately 1000K (1341F). Liquid N_2H_4 at a pressure of approximately 1380 kN/m^2 (200 psia) is injected into the N_2H_4 Catalytic Dissociator thru a capillary opening in the header assembly having a diameter of 0.05 cm (0.020 in). The diameter of the capillary opening is smaller than the quenching diameter for N_2H_4 to prevent propagation of reaction back to the feed tanks.

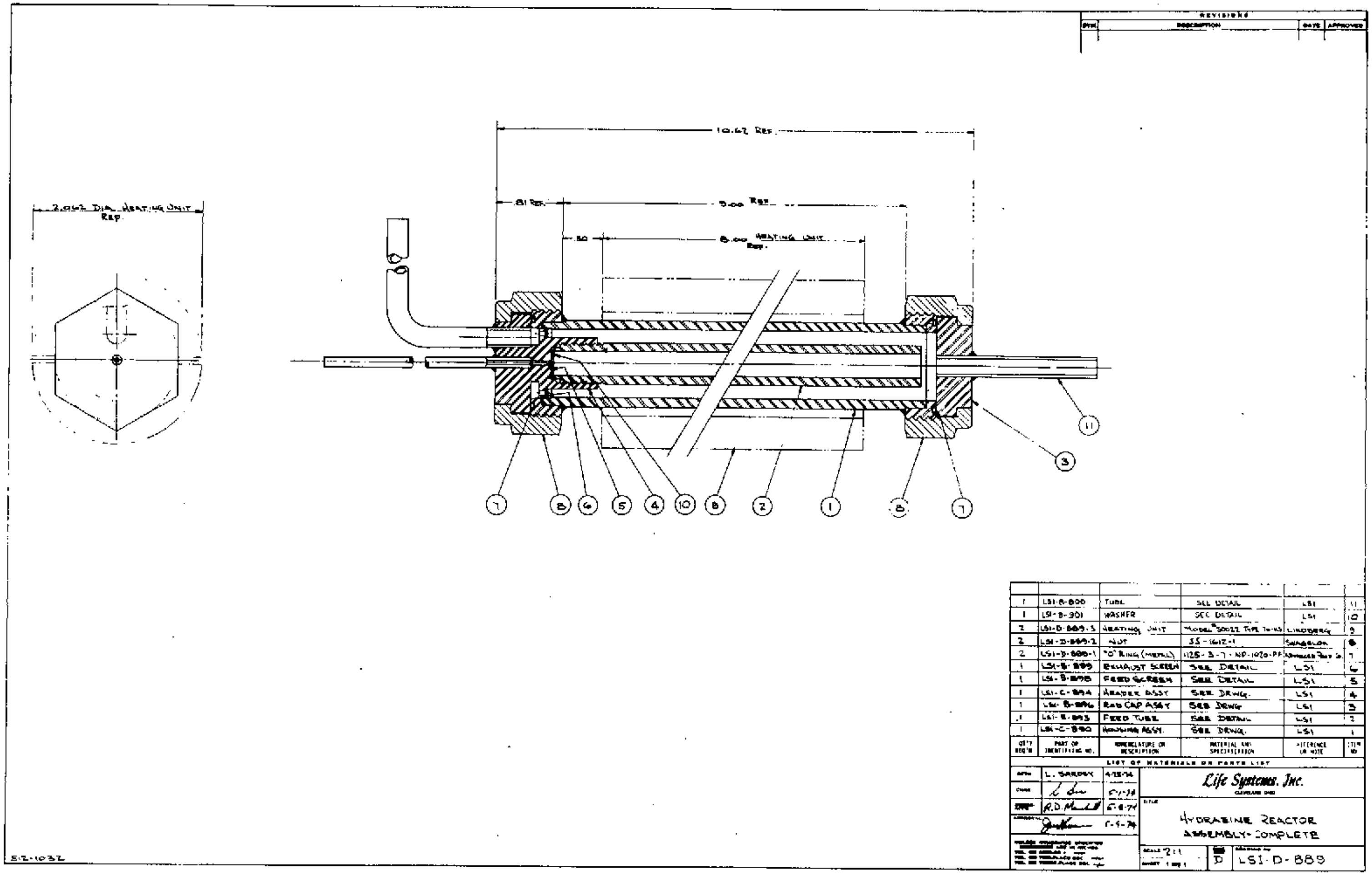
A platinum (Pt) screen is placed at the end of the capillary feed tube. Hydrazine decomposes spontaneously over the screen catalyst to NH_3 and N_2. Approximately 20-40% of the NH_3 formed decomposes instantaneously to N_2 and H_2. Due to the highly exothermic decomposition of N_2H_4 this zone is at the highest temperature in the reactor. The decomposition reactions can be summarized as follows:(4)

Pt Screen: $2N_2H_4 = 2NH_3 + N_2 + H_2$ (3)

Catalyst Bed: $2NH_3 = N_2 + 3H_2$ (4)

Overall: $2N_2H_4 = 2N_2 + 4H_2$ (5)

The Pt catalyst screen also acts as a retaining screen for the packed catalyst bed and therefore prevents plugging of the feed tube. The product gases (NH_3, N_2, and H_2) now flow in the central tube. Ammonia is dissociated to N_2 and H_2 in the endothermic step described in Equation 4. At the end of the central tube the flow pattern of the product gases is reversed in direction. The product gases flow in the annular housing concentric with the central tube and exit at the hottest zone in the reactor. The decomposition of NH_3 to N_2 and H_2 is favored kinetically and thermodynamically at higher temperatures. The "hairpin" type reactor will therefore result in higher NH_3 conversion efficiency. The catalyst retaining screen prevents catalyst particles from being removed by the product gases.



QTY REQ'D	PART OR IDENTIFYING NO.	NOMENCLATURE OR DESCRIPTION	MATERIAL AND SPECIFICATION	REFERENCE OR NOTE	ITEM NO.
1	LSI-B-900	TUBE	SEE DETAIL	LSI	11
1	LSI-B-901	WASHER	SEE DETAIL	LSI	10
2	LSI-D-889-3	HEATING UNIT	MODEL 50022 TYPE 1-15	LINDBERG	9
2	LSI-D-889-2	NUT	SS-1612-1	SWAGELOK	8
2	LSI-D-889-1	"O" RING (METAL)	U25-3-7-NP-1020-PF	[illegible]	7
1	LSI-B-899	EXHAUST SCREEN	SEE DETAIL	LSI	6
1	LSI-B-898	FEED SCREEN	SEE DETAIL	LSI	5
1	LSI-C-894	HEADER ASSY	SEE DRWG.	LSI	4
1	LSI-B-896	END CAP ASSY	SEE DRWG.	LSI	3
1	LSI-B-893	FEED TUBE	SEE DETAIL	LSI	2
1	LSI-C-890	HOUSING ASSY.	SEE DRWG.	LSI	1

LIST OF MATERIALS OR PARTS LIST

DRN	L. SARDOV	4-15-74
CHKD		5-1-74
ENGR	R.D. M	5-8-74
APPROVAL		5-9-74

Life Systems, Inc.
CLEVELAND OHIO

TITLE
HYDRAZINE REACTOR
ASSEMBLY-COMPLETE

SCALE 2:1
SHEET 1 OF 1
SIZE D
DRAWING NO. LSI-D-889

FIGURE 31 HYDRAZINE CATALYTIC DISSOCIATOR SCHEMATIC

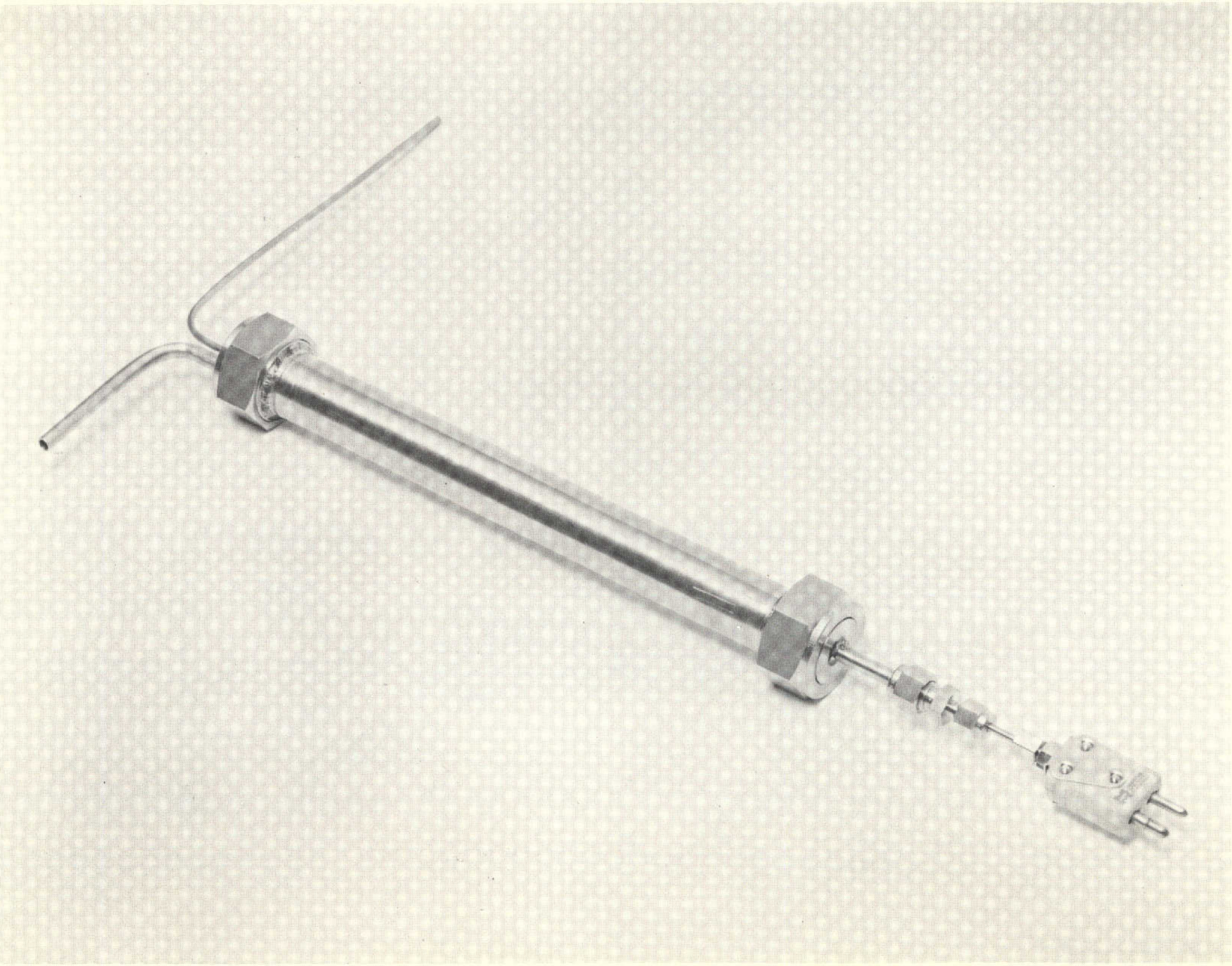


FIGURE 32 N_2H_4 CATALYTIC DISSOCIATOR (ASSEMBLED)

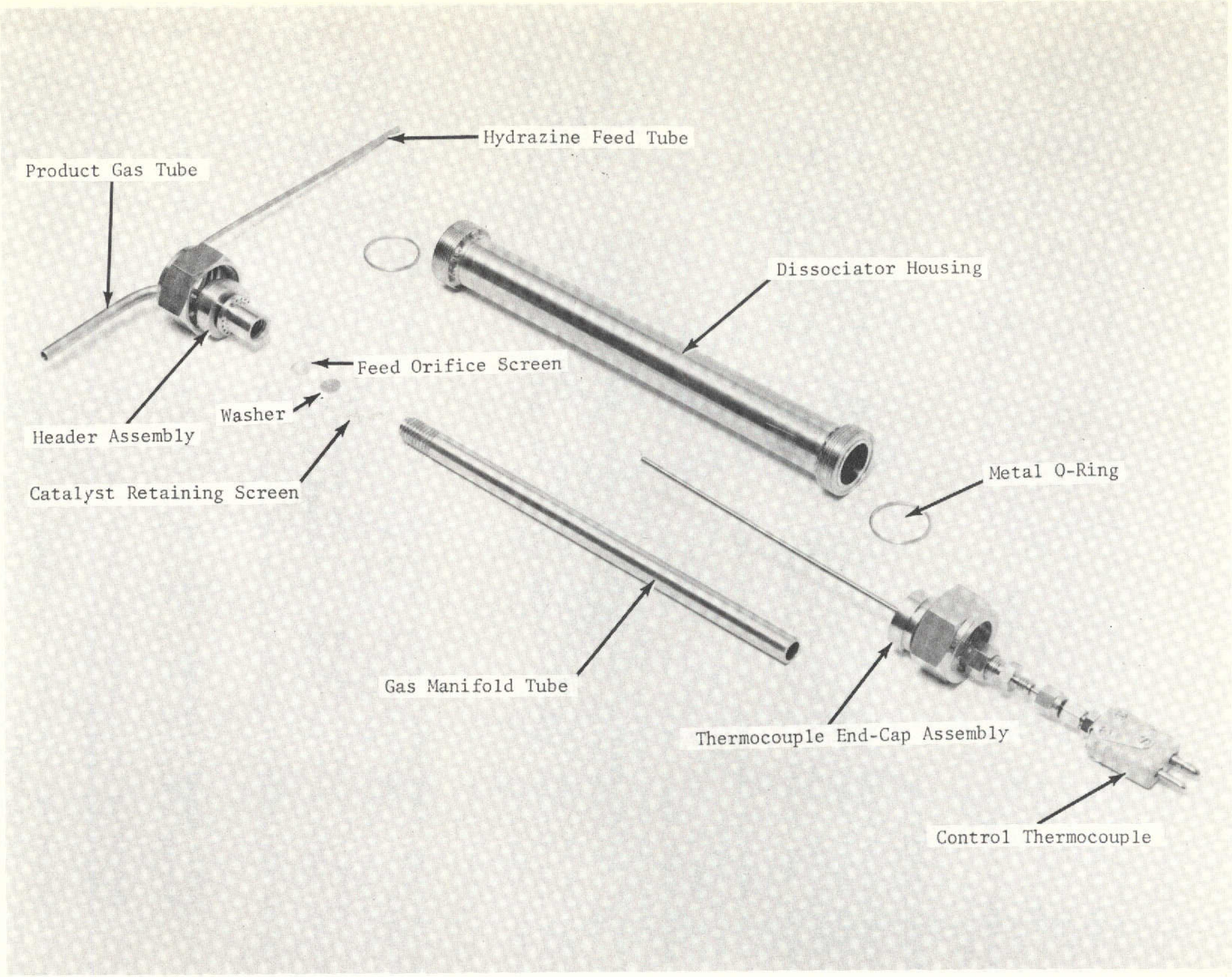


FIGURE 33 N_2H_4 CATALYTIC DISSOCIATOR (DISASSEMBLED)

Equilibrium Constraints

The catalytic dissociation of N_2H_4 proceeds until thermodynamic equilibrium at the temperature and pressure level in the reactor is reached. The critical parameter is the concentration of NH_3 in the product gas stream at equilibrium. Figure 34 shows the concentration of NH_3 as a function of temperature and pressure(5). The NH_3 concentration increases with increasing pressure and decreasing temperature. The curves in Figure 34 represent the lowest NH_3 concentration attainable.

Materials Selection

At 1000K (1341F) and approximately 1379 kN/m^2 (200 psia), there are very few materials which are compatible with N_2H_4 and its decomposition products. This incompatibility is manifested in H_2 embrittlement, nitridification, or NH_3 corrosion, and results in reduced material properties and operating life.

The noble metals, rhenium (Re), molybedenum (Mo), 310 SS, a nickel (Ni) alloy containing 57% Ni, 12% chromium (Cr), and 1.7% tungsten (W), and W are compatible with N_2H_4 and its decomposition products. The high cost of noble metals and Re prohibits their use. Molybdenum is easily oxidized at elevated temperatures. The Ni alloy is not readily available. Tungsten stock of the size required for the reactor is not readily available, expensive, and hard to machine (as compared to 310 SS). The 310 SS was therefore selected by elimination as the material of construction for the N_2H_4 Catalytic Dissociator. Other desirable characteristics of 310 SS are its low thermal conductivity, low heat capacity, and low coefficient of thermal expansion.

Catalyst Selection

A dual catalyst configuration was selected for use in the N_2H_4 Catalytic Dissociator(6). The first catalyst is a Pt screen located at the dissociator N_2H_4 injection port. The N_2H_4 immediately dissociates into NH_3, N_2, and H_2 at the Pt screen. The remaining catalyst bed serves as an NH_3 dissociator. For the second catalyst it was therefore desired to have an NH_3 dissociation catalyst.

A survey of available NH_3 dissociation catalysts established two basic catalyst groups:

1. Noble metal catalysts (iridium (Ir) or rhodium (Rh) on alumina) having a high activity, short life, and high cost.
2. Non-noble metal catalysts (iron (Fe) or alumina) having low activity, long life, and low cost.

At high temperatures the catalytic dissociation rates are very high and gas film resistance to mass transfer is likely to control the reaction rate. The rate controlling step then is the diffusion of NH_3 from the bulk to the catalyst surface. The NH_3 molecule is dissociated as soon as it hits the catalytic surface and reaches equilibrium instantly.

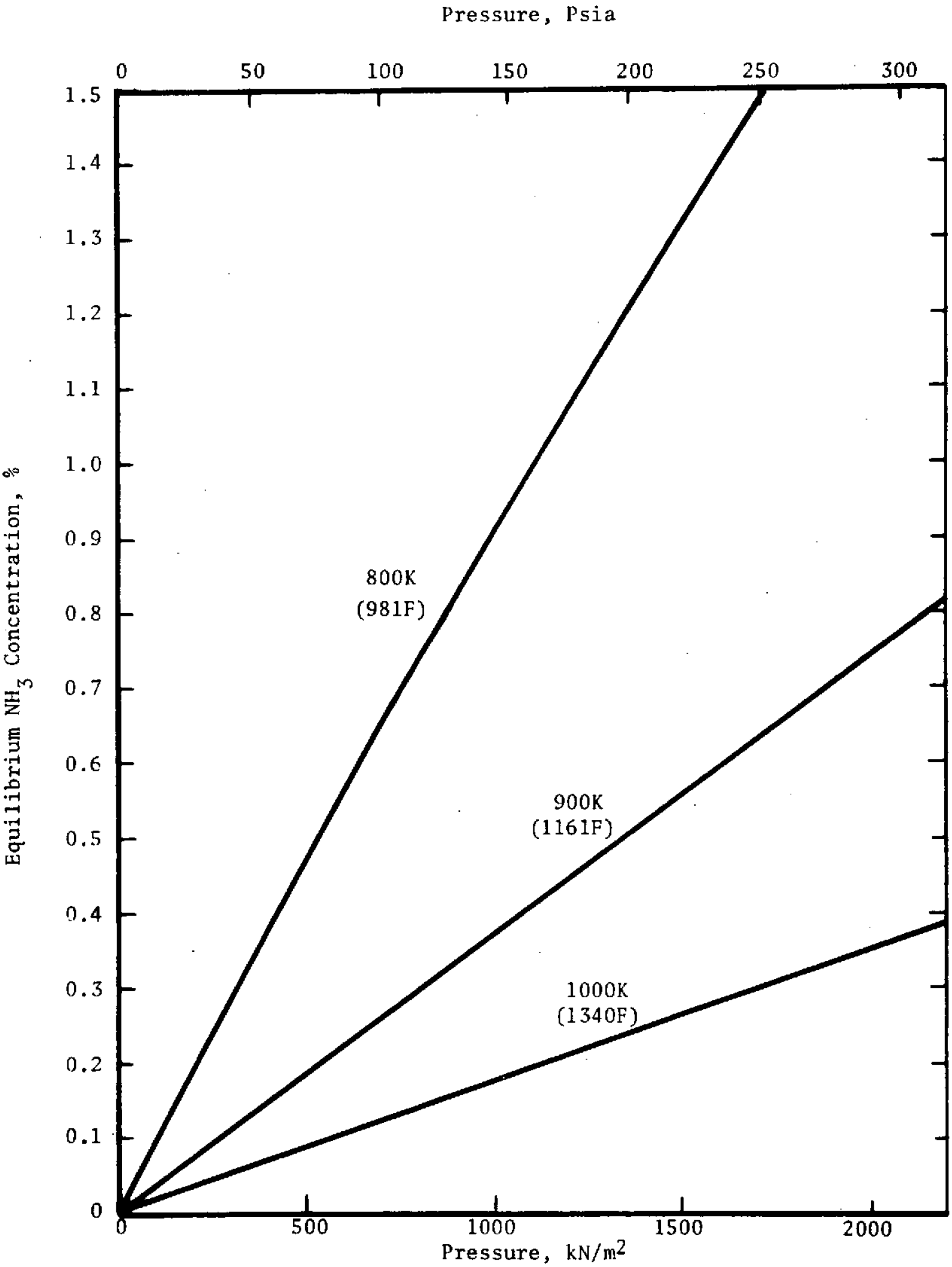


FIGURE 34 EFFECT OF PRESSURE AND TEMPERATURE ON EQUILIBRIUM NH_3 CONCENTRATION

Under these conditions the activity of catalyst is not of paramount importance. The criteria of maximum resistance to degradation in catalytic activity caused by physical attrition or contamination is more important. A doubly promoted, Fe on alumina catalyst (Haldor-Topsoe catalyst HT-KMIR) was selected as the NH_3 dissociation catalyst on the basis of long catalyst life, low catalyst bed pressure drop, and low cost.

System Design

Table 11 lists the design specifications for the N_2H_4 Catalytic Dissociator. A photograph of the system as integrated and tested with the GSA is presented in Figure 35. The system consists of the mechanical components assembly and the instrumentation package.

Mechanical Design and Operation

The system schematic is presented in Figure 36. Hydrazine is fed under pressure (approximately 1379 kN/m^2 (200 psia)) at room temperature into the system through SV1. A porous stainless steel filter upstream of SV1 is used to prevent particles from clogging the flow control orifice and to prevent flame propagation back from the N_2H_4 Catalytic Dissociator to the N_2H_4 storage tanks. The flow control orifice is installed directly into the solenoid valve fitting. Flow is controlled across the orifice by manually adjusting the N_2H_4 feed pressure from the GSA. The N_2H_4 enters the N_2H_4 Catalytic Dissociator and is catalytically dissociated into N_2, H_2, and a trace of NH_3. Product gas exits the N_2H_4 Catalytic Dissociator at approximately 1000K (1340F). A gas-to-gas (air) heat exchanger is used to lower the temperature of the product gases to less than 322K (120F) prior to leaving the system. A sample tap is provided on the N_2/H_2 exhaust stream to analyze the exhaust gases for NH_3, N_2, and H_2 concentrations. System pressure is controlled by ground support using a backpressure regulator during nonintegrated operation. Upon integration with the N_2H_2 Separator System, however, backpressure regulation would be provided by the N_2/H_2 Separator System itself. The approximate operating pressure of the exhaust gases would be 1034 - 1379 kN/m^2 (150 - 200 psia).

The system is equipped with an automatic N_2 purge which is initiated following a shutdown. During actual running, the N_2 purge solenoid valve (SV2) is closed as is the purge vent solenoid valve (SV4). A shutdown causes SV2 and SV4 to open. System pressure decays slowly across the orifice located downstream of SV4. When the pressure decays to below the purge pressure, the check valve downstream of SV2 permits N_2 purge gas to enter the system. The purging operation continues until manually ended. The orifice on the purge vent line maintains the system under positive pressure to prevent ambient air from entering the system. A second vent solenoid valve (SV3) is provided to manually purge the system during startup at a faster volumetric flow rate than allowed by the orifice.

Instrumentation Design

Instrumentation is provided to:

1. Control N_2H_4 Catalytic Dissociator temperature (TC1) and cooling fan voltage.

TABLE 11 HYDRAZINE CATALYTIC DISSOCIATOR DESIGN SPECIFICATIONS

N_2H_4 Feed	
Source	Liquid N_2H_4
Flow Rate	
Nominal, kg/d (Lb/Day)	7.78 (17.14)
cm^3/min	5.4
Minimum, kg/d (Lb/Day)	3.6 (8.0)
cm^3/min	2.5
Maximum, kg/d (Lb/Day)	8.2 (18.0)
cm^3/min	5.7
Composition (Weight)	
N_2H_4, %	98 - 100
Water, %	0 - 2
Temperature, K (F)	293 - 298 (68 - 77)
Pressure (above product gas pressure)	
Nominal, kN/m^2 (Psia)	276 (40)
Minimum, kN/m^2 (Psia)	69 (10)
Maximum, kN/m^2 (Psia)	345 (50)
Product Gas	
Flow Rate	
Nominal, kg/d (Lb/Day)	7.78 (17.14)
dm^3/min (Slpm)	12.2 (12.2)
Minimum, kg/d (Lb/Day)	3.6 (8.0)
dm^3/min (Slpm)	5.7 (5.7)
Maximum, kg/d (Lb/Day)	8.2 (18.0)
dm^3/min (Slpm)	12.8 (12.8)
Composition (by volume)	
N_2, %	32 - 34
H_2, %	66 - 68
NH_3, %	0 - 1.0
Water, %	0 - 0.7

continued-

Table 11 - continued

Temperature	
Minimum, K (F)	298 (77)
Maximum, K (F)	700 (800)
Pressure	
Nominal, kN/m^2 (Psia)	1346 (195)
Minimum, kN/m^2 (Psia)	1104 (160)
Maximum, kN/m^2 (Psia)	2070 (300)
<u>Electrical Power</u>	
Supply Voltage, VDC	28±4
Supply Voltage, VAC	115±10
Hz	60
<u>Purge Supply</u>	
Type Gas	N_2
Pressure, kN/m^2 (Psia)	310 (45)
<u>Coolant Supply</u>	
Type	Air
Temperature, K (F)	293 - 298 (68 - 77)

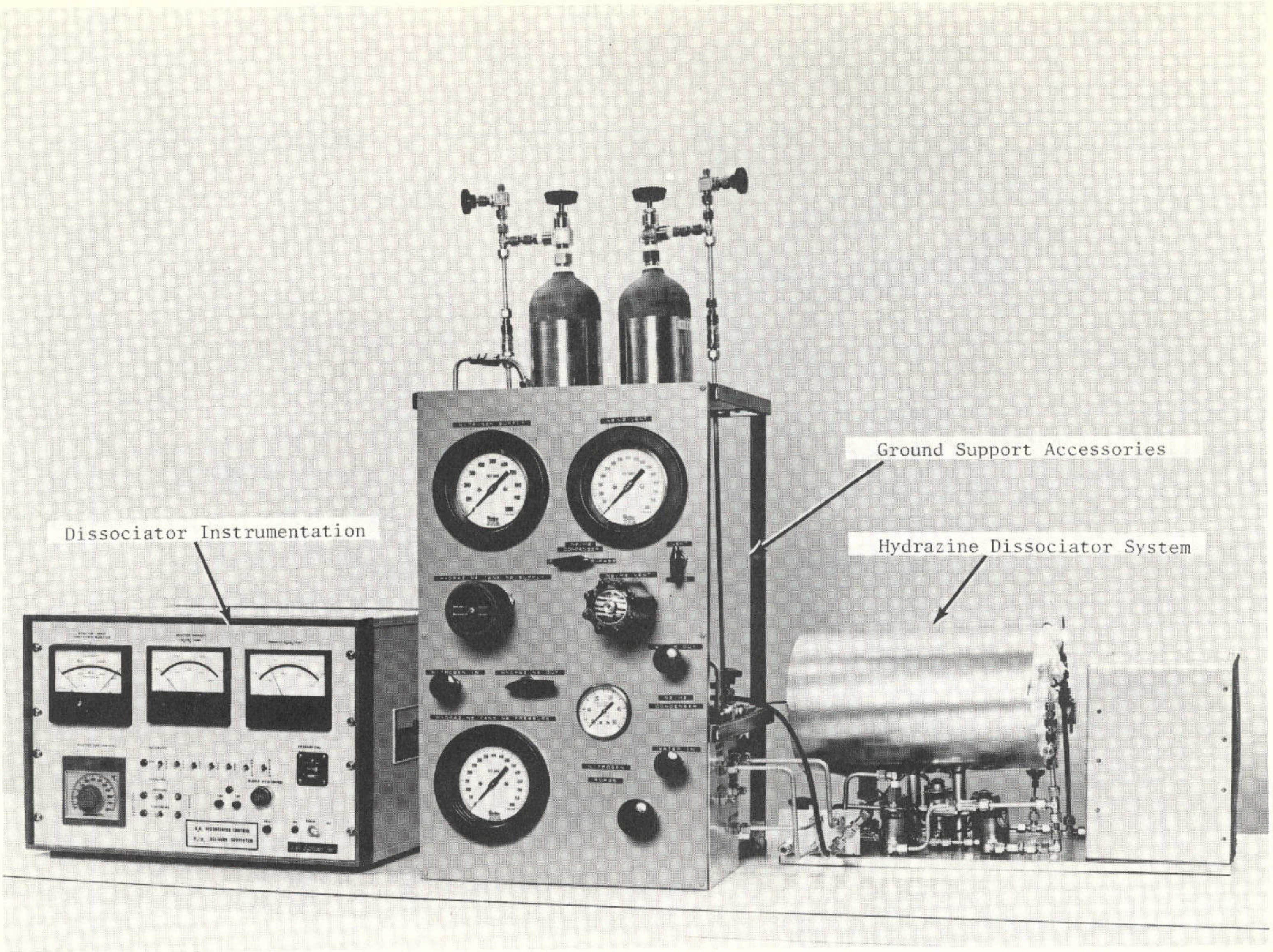


FIGURE 35 HYDRAZINE CATALYTIC DISSOCIATOR TEST FACILITY

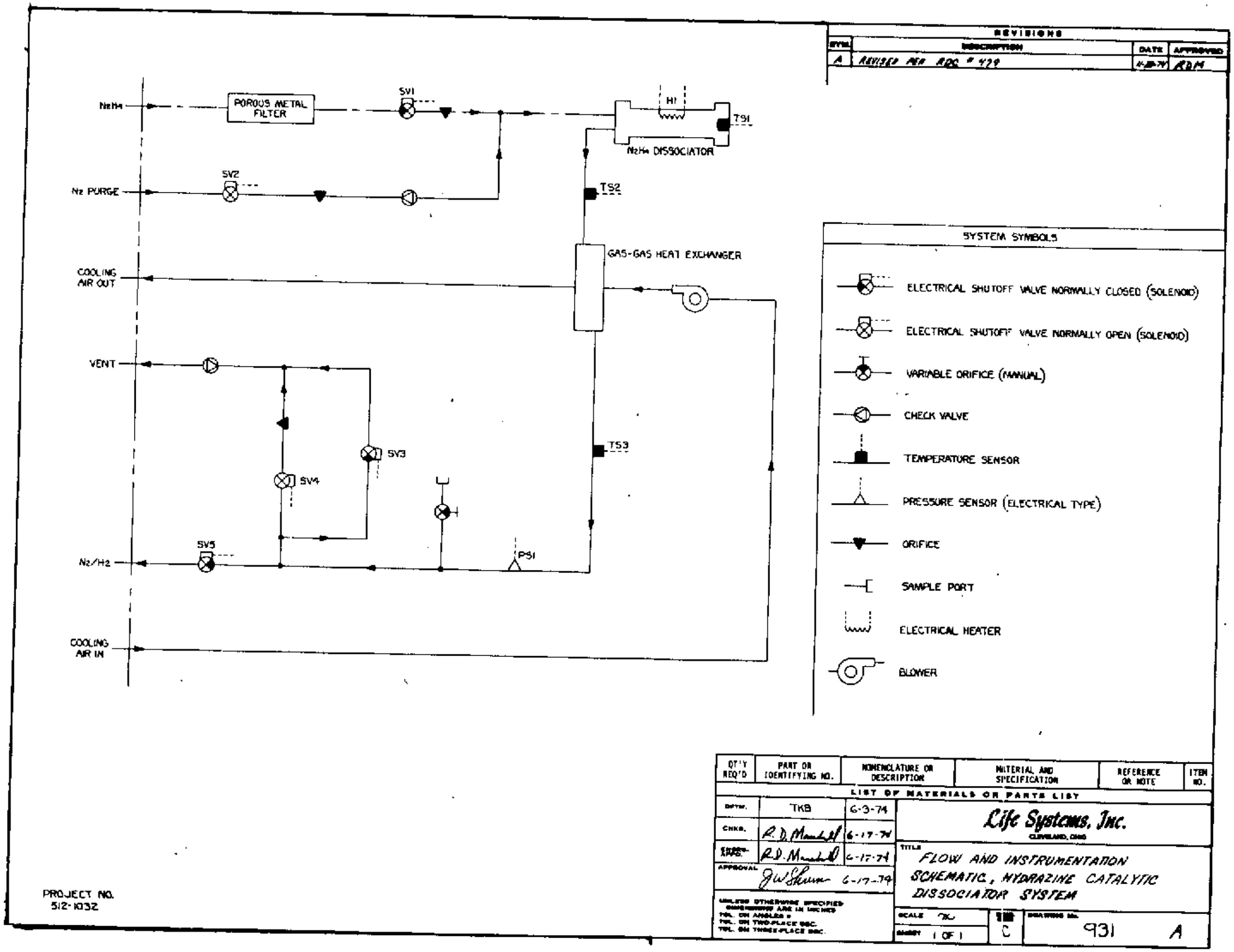


FIGURE 36 HYDRAZINE CATALYTIC DISSOCIATOR SYSTEM SCHEMATIC

2. Monitor system temperatures.
3. Provide power to the solenoid valves, the heater/controller, and the cooling fan.
4. Shutdown the system for excessive pressure and temperature.

Laboratory breadboard-style instrumentation was selected for maximum testing flexibility and direct readout of system parameters in engineering units.

Control Features. The following control features were incorporated:

1. Automatic fail-safe shutdown and N_2 purge initiated by excessive reactor temperature and pressure.
2. Startup is accomplished by supplying power to SV1, SV2, SV4, SV5, the cooling fan, and the heater/temperature controller. Shutdown is accomplished by removing power from these components.
3. Fan speed (voltage) is manually set by a digital potentiometer.
4. Hydrazine Catalytic Dissociator temperature is maintained by a temperature controller.

Monitoring Features. The following monitoring features were incorporated:

1. Continuous monitoring and direct readout for system temperatures (TS1, TS2, and TS3) is provided.
2. Temperature shutdown is signalled by TS1, pressure shutdown by a pressure switch (PS1).

Ground Support Accessories

Ground Support Accessories were required to:

1. Supply N_2H_4.
2. Supply purge N_2.
3. Vent the system during shutdown and N_2 purge.
4. Vent N_2/H_2 product gas.

Figure 37 is a schematic of the GSA for the N_2H_4 Catalytic Dissociator. The N_2H_4 feed pressure is controlled by the GSA thereby controlling the N_2H_4 flow rate across the system's feed orifice. This pressure control is accomplished by controlling the N_2 pressure on the top of the N_2H_4 storage tanks. Two N_2H_4 storage tanks are provided to allow one to be refilled without interrupting system operation.

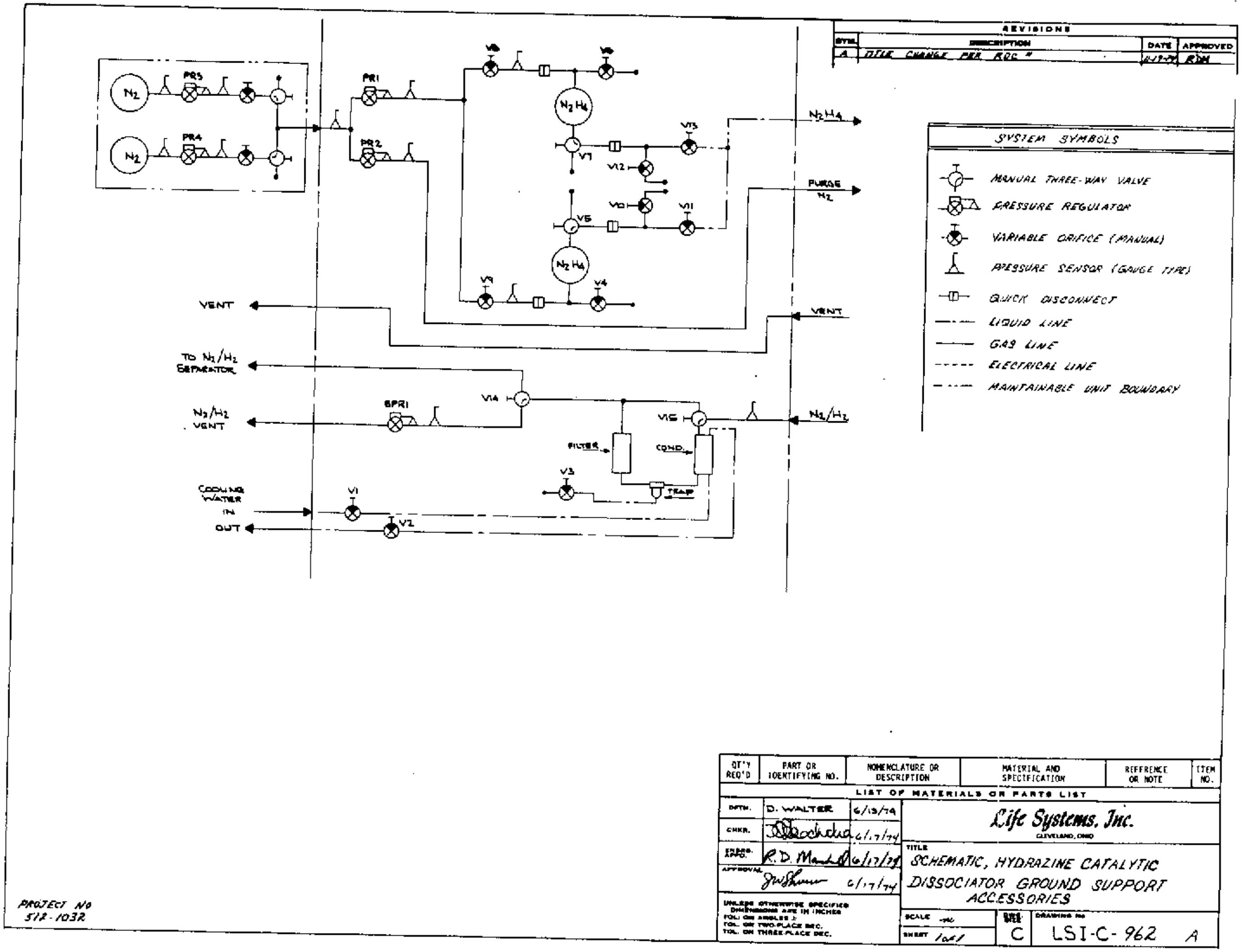


FIGURE 37 HYDRAZINE CATALYTIC DISSOCIATOR GSA SCHEMATIC

Purge N_2 is supplied to the system at 310 kN/m^2 (45 psia). The purge vent allows the product and purge gases to be vented away from the test facility upon system shutdown.

The N_2/H_2 product gas from the reactor enters the GSA and can either be bypassed directly for separation or vented. Normal operation is to vent. The GSA simulates the interface with a separator system by controlling the product gas pressure with a backpressure regulator (BPR1). A condenser, trap filter arrangement is provided to protect BPR1 from possible NH_3 contamination.

Test Program

The N_2H_4 Catalytic Dissociator System Test Program consisted of system shakedown testing, parametric testing to determine the effect of temperture, pressure, and N_2H_4 flow rate on dissociator performance, and a 100-hour DVT to determine the effect of time on dissociator performance. In addition, component checkout and calibration tests were completed.

Shakedown Test

A system Shakedown Test was run to verify the integrated system and GSA operation. The shakedown testing included catalyst activation with H_2 at an elevated temperature, verifying startup and N_2H_4 tank refill procedures, and inducing temperature and pressure shutdowns to verify fail-safe operation. Two modifications were made as a result of the shakedown testing:

1. The GSA purge N_2 pressure regulator failed and was replaced by an orifice.

2. The temperature controller was set approximately 50K (90F) below the desired temperature to allow for overshoot caused by the highly exothermic reaction.

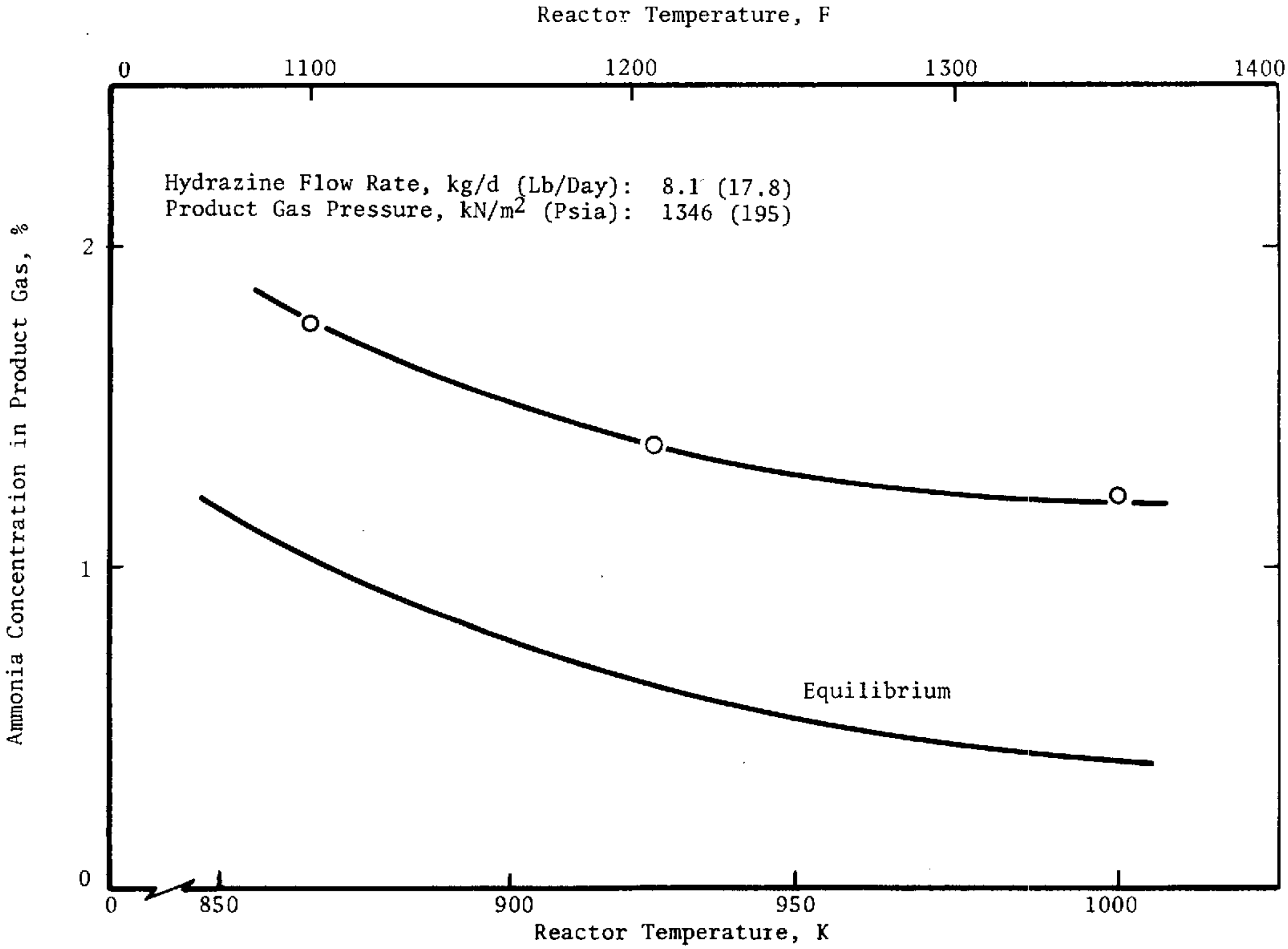
Effect of Temperature

The N_2H_4 Catalytic Dissociator performance, as measured by the NH_3 concentration in the product gas stream, was determined as a function of temperature from 866K (1100F) to 1005K (1350F). The results of the test and the equilibrium curve are presented in Figure 38. The experimental curve followed the shape of the equilibrium curve. The equilibrium curve represents the best attainable results.

Effect of Pressure

The N_2H_4 Catalytic Dissociator performance, as measured by NH_3 concentration in the product gas stream, was determined as a function of pressure from 207-1829 kN/m^2 (30-265 psia). The results of the test and the equilibrium curve are presented in Figure 39.

The decomposition of NH_3 to N_2 and H_2 is favored thermodynamically at lower pressures. The experimental data indicates, however, that NH_3 concentration



Hydrazine Flow Rate, kg/d (Lb/Day): 8.1 (17.8)
Product Gas Pressure, kN/m^2 (Psia): 1346 (195)

FIGURE 38 EFFECT OF REACTOR TEMPERATURE ON PRODUCT NH_3 CONCENTRATION

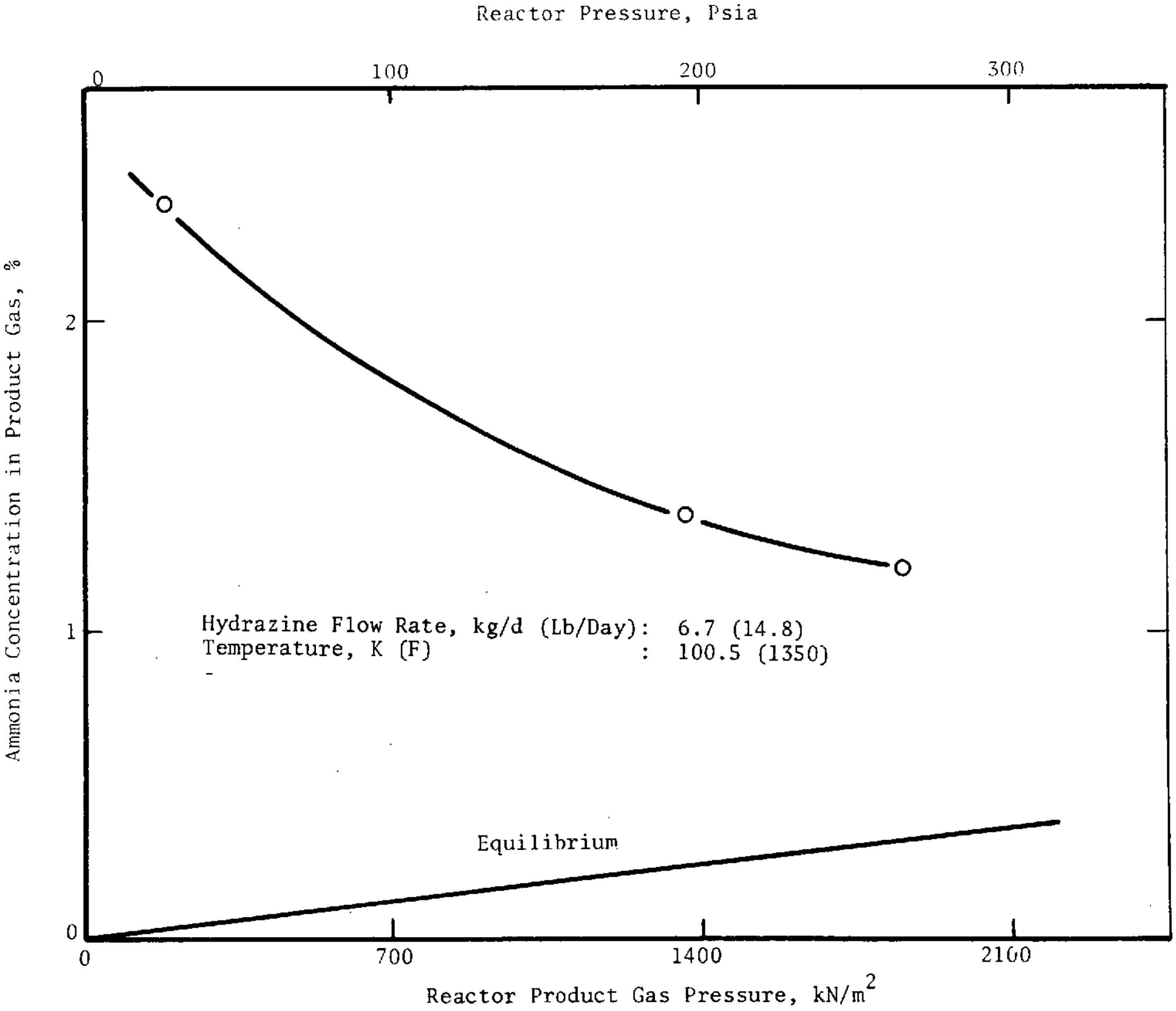


FIGURE 39 EFFECT OF REACTOR PRODUCT GAS PRESSURE ON NH_3 CONCENTRATION

decreases with increasing pressure. The following rationale was used to explain this apparent discrepancy.

The rate limiting step is the diffusion of NH_3 through the gas diffusion film to the surface of the catalyst. The NH_3 concentration at the catalyst surface then is the equilibrium concentration of NH_3 at the catalyst surface temperature. The driving force for NH_3 transfer to the catalyst surface from the reactant gas stream is the NH_3 partial pressure (pNH_3) gradient. An increase in the product pressure increases pNH_3 and hence the driving force resulting in a higher reaction rate. At higher pressures the surface will become increasingly saturated with NH_3 molecules. If these do not react rapidly enough, surface reaction becomes controlling causing the reaction rate to level off.

Effect of N_2H_4 Flow Rate

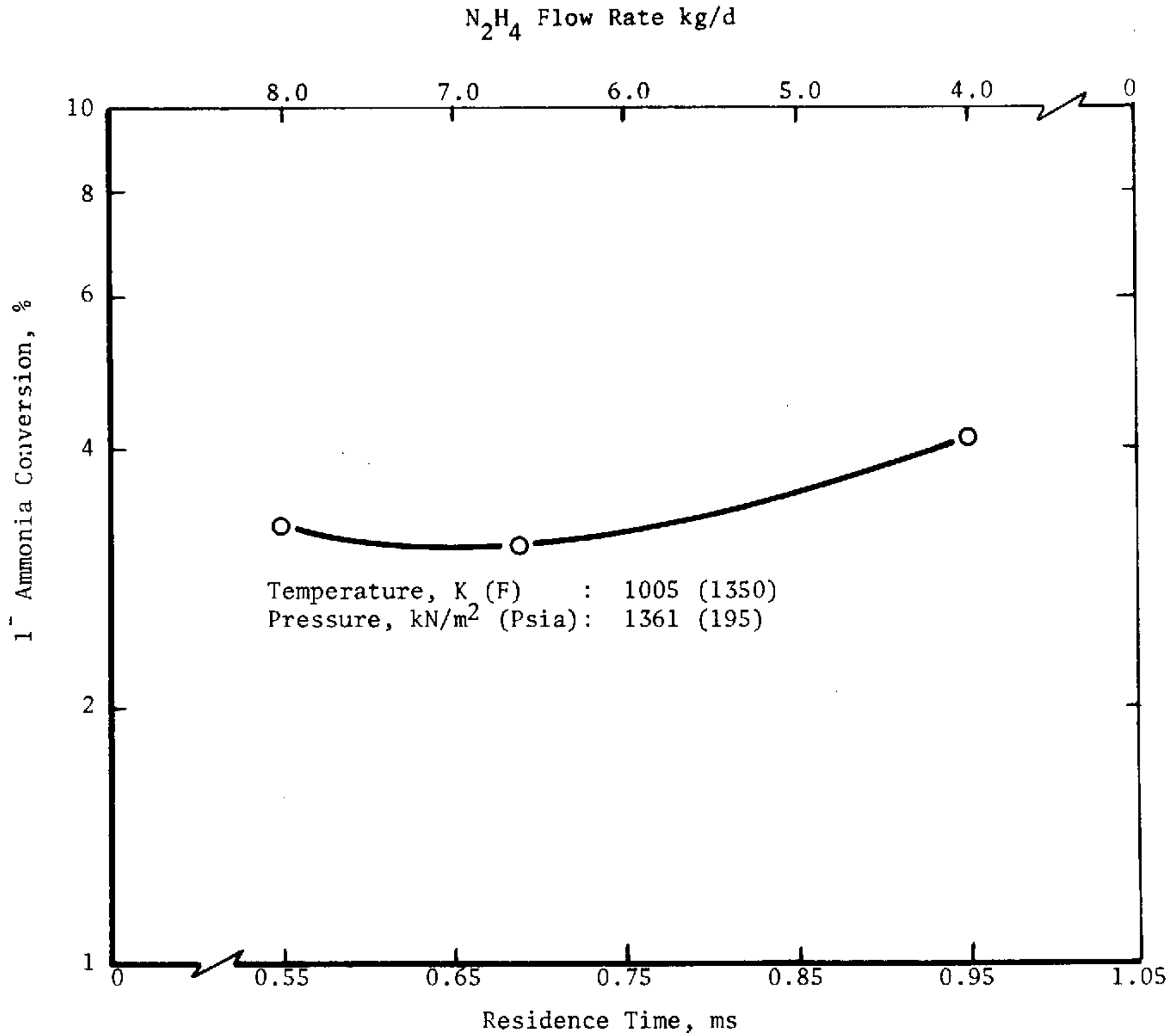
The effect of N_2H_4 flow rate (and hence residence time on N_2H_4 Catalytic Dissociator performance) as measured by the percent of NH_3 not dissociated, was determined for 4-8 kg/d (8.8-17.6 lb/day), i.e., a residence time of 0.55-0.95 seconds. The results of the experiment are presented in Figure 40.

The highest NH_3 conversion was obtained at 7.0 kg/d (15.4 lb/day). At higher N_2H_4 flow rates lower NH_3 conversion was observed in spite of favorable NH_3 mass transport to the catalyst surface. It appears that the favorable mass transfer of NH_3 was more than counterbalanced by the decrease in residence time. This would suggest that to obtain about 0.5% NH_3 (98.93% NH_3 conversion) longer bed lengths are needed. At lower N_2H_4 loadings the positive effect of longer residence times is more than counterbalanced by poorer mass transfer rates for NH_3. The above two effects suggest that reactor cross-section should be decreased and the bed length increased to improve performance.

Design Verification Test

The effect of time on the N_2H_4 reactor performance was observed during a continuous 100-hour DVT. The concentration of NH_3 in the reactor products and the degree of NH_3 dissociation (NH_3 conversion) over the 100-hour period are plotted in Figure 41. The operating conditions for the test are listed in Table 12. High NH_3 concentrations in the reactor products are a result of lower NH_3 conversion. Ammonia conversion is calculated from the N_2/H_2 ratio and is very sensitive to the N_2/H_2 ratio. Third decimal place changes in the N_2/H_2 ratio result in significant first decimal place changes in NH_3 conversion. The consistency of NH_3 conversion data is therefore somewhat limited by the accuracy in the analysis of N_2 and H_2 in the reactor product gas.

A trend towards higher NH_3 concentration with time was observed. This could result from the physical or chemical degradation of the catalyst with time. The optimum temperature for the NH_3 synthesis Haldor-Topsoe KMIR H_2-reduced catalyst used in the N_2H_4 reactor is around 823K (1022F). At this temperature a catalyst life in excess of three years is suggested by manufacturer literature to yield equilibirum concentrations of less than 0.5% NH_3 in the N_2/H_2 product. The N_2H_4



Temperature, K (F) : 1005 (1350)
Pressure, kN/m^2 (Psia): 1361 (195)

FIGURE 40 EFFECT OF RESIDENCE TIME (N_2H_4 FEED RATE) ON AMMONIA CONVERSION

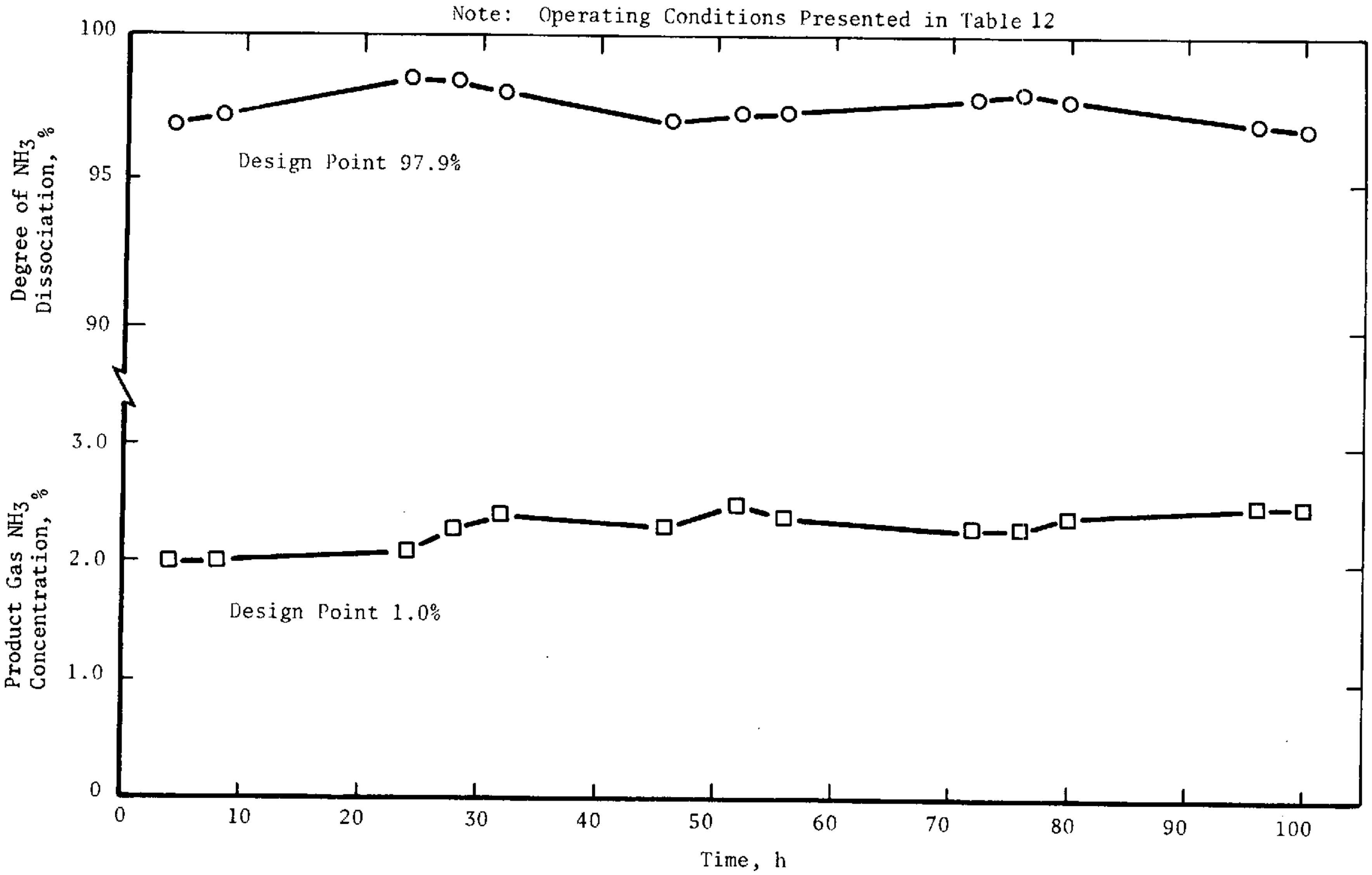


FIGURE 41 EFFECT OF TIME ON HYDRAZINE CATALYTIC DISSOCIATOR PERFORMANCE

TABLE 12 N_2H_4 CATALYTIC DISSOCIATOR OPERATING CONDITIONS

N_2H_4 Feed	
Flow Rate, kg/d (Lb/Day)	8.00 - 8.07 (17.6 - 17.8)
dm^3/min	5.54 - 5.60
Composition (by weight)	
N_2H_4, %	99.3
Water, %	0.4
Other	0.3
Temperature, K (F)	21.1 - 22.2 (70 - 72)
N_2/H_2 Product	
Flow Rate, kg/d (Lb/Day)	8.00 - 8.07 (17.6 - 17.8)
dm^3/min (Slpm)	12.5 - 12.6 (12.5 - 12.6)
Composition (by volume)	
N_2, %	32.7 - 32.9
H_2, %	64.8 - 65.1
NH_3, %	2.0 - 2.5
Water, %	0.18 - 0.21
Temperature, K (F)	20.0 - 22.2 (68 - 72)
Pressure, kN/m^2 (Psia)	1326 - 1396 (190 - 200)
N_2H_4 Dissociator	
Temperature, K (F)	1000 - 1005 (1340 - 1350)

reactor was maintained at 1000K (1350F) during the DVT. At these higher temperatures some of the catalytic activity is lost, however, the catalyst was expected to operate without much further loss in activity for at least a year(7).

SUPPORTING TECHNOLOGY

A literature and product survey was conducted to establish simple and cost-effective procedures to analyze gas streams for N_2, H_2, NH_3, and N_2H_4 concentrations for the N_2H_4 Catalytic Dissociator, Pd/Ag Separator, and Polymer-Electrochemical Separator testing. Analysis techniques were required to detect and analyze the following:

1. Trace quantities of N_2H_4 (less than 1%) in the N_2H_4 Catalytic Dissociator product gas.
2. Trace quantities of NH_3 (less than 5%) in the N_2H_4 Catalytic Dissociator product gas.
3. Nitrogen contamination (less than 2%) of N_2/H_2 Separator H_2 product gas.
4. Hydrogen contamination (less than 2%) of N_2/H_2 Separator N_2 product gas.

The following analytical systems were evaluated for the application.

1. Gas Chromatograph.
2. Infrared Analyzers.
3. Mass Spectrometer.
4. Analytical Conductivity Analyzers.
5. Wet Methods.
    a. Orsat analyzers with adsorbent for H_2 removal.
    b. Orsat analyzers with copper oxide (CuO) tube for H_2 removal.
    c. Bendix self-reading detector tubes for 82 different gases and vapors.
6. Ultrasonic Detector Analyzers.
7. Ultraviolet Spectroscopy.
8. Nuclear Magnetic Resonance Spectroscopy.
9. Electron Spin Resonance Spectroscopy.

Alternate Methods Evaluated

The gas chromatograph was selected for the present application by evaluating, comparing, and eliminating the other methods with respect to the gas chromatograph.

Infrared Analyzers

The region commonly used in infrared instrumentation is 1.0 to 25.0 µm (3.7-91.5 x 10^{-6} in). With a few exceptions all molecules adsorb energy in various portions of this range. Elemental gases such as O_2, N_2, H_2, and chlorine (Cl_2) and the rare gases do not adsorb energy in this portion of the infrared spectrum and hence they cannot be measured by ordinary infrared techniques. Ammonia and N_2H_4 can, however, be accurately measured by infrared analysis.

The disadvantages of the infrared analyzer are:

1. Infrared analyzers cannot analyze N_2 or H_2.
2. The system is accurate over small ranges of constituent concentration and thus requires a separate instrument calibrated for each concentration range.

Mass Spectrometer

Mass spectrometers analyze substances according to the mass-to-charge ratio of the constituent atoms, groups of atoms or molecules present. Nearly all mass spectroscopes accelerate and detect only the positively charged ions. By using a combination of electric and magnetic fields, the various ions are separated according to their specific mass. Ions of any desired mass are made to pass through a fine slit and strike an ion collector which measures the intensity of the ion ray. The instrument can be calibrated to read directly the percentages of the various species proportional to the intensity of the rays.

The disadvantages of the mass spectrometer are:

1. The system is highly sophisticated and requires great skill in maintenance, operation, and interpretation.
2. The spectrometer tube which is the heart of the instrument's ionization chamber is prone to poisoning, damage, and is very expensive to replace.
3. Wet NH_3 corrosion of the spectrometer tube may occur.

Analytical Conductivity Analyzers

Conductivity analyzers measure and compare the thermal conductivities of a gas sample and a gas of known purity. Heated wires, carrying equal currents, are suspended in the two gases. These wires form two legs of a Wheatstone bridge circuit. Since the heat conductivities of gases vary, the wires are cooled unequally. As electrical resistance varies with changes in temperature, the conductivities of the wires are changed and the system is unbalanced. The difference in current values across the bridge circuit or "imbalance" is read directly on a DC potentiometer.

The disadvantages of the analytical conductivity analyzer are:

1. Analytical conductivity analyzers are capable of analyzing only one component in a gas mixture.
2. The system is accurate only over small concentration ranges and would require a separate calibration for each range.

Wet Methods

Wet methods are generally inferior to the techniques already outlined. Orsat analyzers using adsorbents or CuO tubes for H_2 removal and analysis are extremely inflexible and almost obsolete. Also, the accuracy obtained from this apparatus is highly subjective.

The following components are removed by direct adsorption in the following order: CO_2, illuminants or unsaturated hydrocarbons, O_2, H_2, CO, and N_2 by difference. The adsorbents for the above analysis are caustic potash, fuming sulfuric acid (H_2SO_4), alkaline pyrogallate solution, heated CuO or Pd catalyst tube and acid cuprous chloride. An adsorbent solution for H_2 is colloidal Pd in sodium protalbinate base.

The Bendix-Kitagawa precision detector tubes are formulated with a constant reagent weight deposited on a fine grain or mesh size inert material, such as silica gel, to ensure uniform flow and distribution. Each reagent is selected so that there is a sharp and distinct color demarcation in the tube caused by one or a group of chemical species present in the sample. The length of the stain obtained by passing a constant volume of a gas sample through the detector tubes are compared to accurately calibrated charts supplied to obtain the concentration of the component.

The disadvantages of the wet methods are:

1. The Orsat apparatus is quite tedious to operate and requires skillful handling and reading of minute changes in gas volume from a 100 ml gas buret.
2. The Orsat apparatus can be used to analyze just a few gases and is thus quite inflexible. The Bendix tubes are subject to interferences from the other component present.
3. The Orsat apparatus takes almost five times as much time to analyze a gas sample as with a chromatograph.

4. The Orsat apparatus cannot be used to analyze water in gas samples.
5. Accuracy of Orsat apparatus and Kitagawa tubes is much lower than that obtained with a mass spectrometer, gas chromatograph, and other analytical techniques.

Ultrasonic Detector Analyzers

Ultrasonic detectors which measure the speed of sound traveling through a gas mixture can be used for quantitative analysis of gas mixtures. As the composition of the gas changes, so does the speed of sound. This property is generally additive on a linear basis, and is predictable and calculable. If helium (He), H_2, or other carrier gas of low mass is used, the detector's response to sample components is proportional to their molecular weight. Since sound measurements can be made with great accuracy and precision, an ultrasonic detector may be well-suited for such an analysis.

The disadvantages of the ultrasonic detector analyzer are:

1. The ultrasonic detectors can be used most effectively for binary mixtures only.
2. The temperature of the detector cell has to be controlled within ±0.001K (0.0018F) because the speed of sound is very sensitive to temperature changes.
3. The detectors are used most effectively to analyze gas streams leaving a chromatographic column and have a sensitivity about 50X greater than thermal conductivity detectors.

Ultraviolet, Nuclear Magnetic Resonance and Electron Spin Resonance Spectroscopy

These systems were evaluated and were quickly eliminated from further consideration. In ultraviolet spectroscopy it was established that N_2 and H_2 do not adsorb ultraviolet radiation appreciably at wavelengths longer than 2.50×10^{-5} cm (1.0×10^{-5} in) and are therefore not measurable. Nuclear magnetic resonance and electron spin resonance spectroscopy techniques are very complicated and great skill and know-how is required to operate such systems. The techniques are more useful for separation and identification of isotopes and various inorganic compounds.

Gas Chromatograph

Gas chromatography is a quick and convenient method of analyzing most gas mixtures. In adsorption chromatography, a gaseous feed mixture is injected in a single pulse into an inert carrier gas stream. The feed mixture components are carried into the adsorbent bed by the carrier gas which is located in a packed column. If the components adsorb to different extents on the adsorbent material, the two species will have different residence times in the column. A species that is more strongly adsorbed will tend to spend a proportionately longer time adsorbed into the stationary solid phase than will a lightly adsorbed species. Consequently, the two species will come out of the end of the column in the effluent carrier gas at different times; the lightly adsorbed components first and the more adsorbed components in ascending order of tendency to adsorb into the solid phase.

Two different techniques were developed for separation and detection of H_2, N_2, NH_3, and N_2H_4 by gas chromatography. The first requires a series-bypass switching, multicolumn technique and is used in conjunction with a Carle AGC-311 Chromatograph. The second requires programmed temperature chromatography and is used in conjunction with a Varian 1720-10 chromatograph. Both chromatographs were used for the analysis.

Series-Bypass Switching, Multicolumn Technique (Carle AGC-311)

This technique is commonly used for chromatographs in which the column temperature cannot be programmed and therefore must be maintained at some suitable constant temperature. Separation and analysis of H_2, N_2, NH_3, and N_2H_4 in multicomponent gas samples requires the multicolumn technique and series-bypass valving configuration illustrated in Figure 42. The combination of a downstream molecular sieve 13X column with a carefully selected upstream column, depending on the sample type, allows the complete quantitative analyses of many gas mixtures otherwise impossible in a single analysis.

The upstream column is a Teflon column packed with 4% Theed on 40-80 mesh Graphon. An inert gas (91.5% He and 8.5% H_2) flows through the instrument at a constant rate. The column bath temperature is set around room temperature. By adjusting the variable restrictors, flow in the left and right columns is matched such that each has roughly 20-30 cc/min (7.1×10^{-4} - 10.6×10^{-4} cfm) of carrier gas flowing through it. The resistance of the flow restrictor parallel to the downstream molecular sieve column is adjusted such that the flow through the right column is the same in both the series and bypass position.

Operation of the series-bypass column configuration is shown in Figure 43. A multicomponent sample containing H_2, N_2, NH_3, and N_2H_4 is injected with a syringe or a gas sample valve into the series-bypass column arrangement with the valve in bypass position (Figure 43b). Two of the gases in the sample (H_2 and N_2) pass through column 1 (Theed) without being separated and are recorded by the thermal conductivity detector (TCD) as a single composite peak. Time required for eluting the composite peak is noted. Ammonia and N_2H_4 are retarded and emerge, fully resolved, soon after the composite peak, as illustrated in Figure 44.

The columns are again set in series position and a sample injected (Figure 2a). After the time required for obtaining the composite peak, the valve is set in bypass position (Figure 43b). Hydrogen and N_2 have now entered the molecular sieve column and are retained there. In the bypass position the upstream column is connected directly to the detector while the NH_3 and N_2H_4 elute (Figure 43c), and the H_2 and N_2 elute. A typical chromatogram obtained by the above analysis is shown in Figure 45.

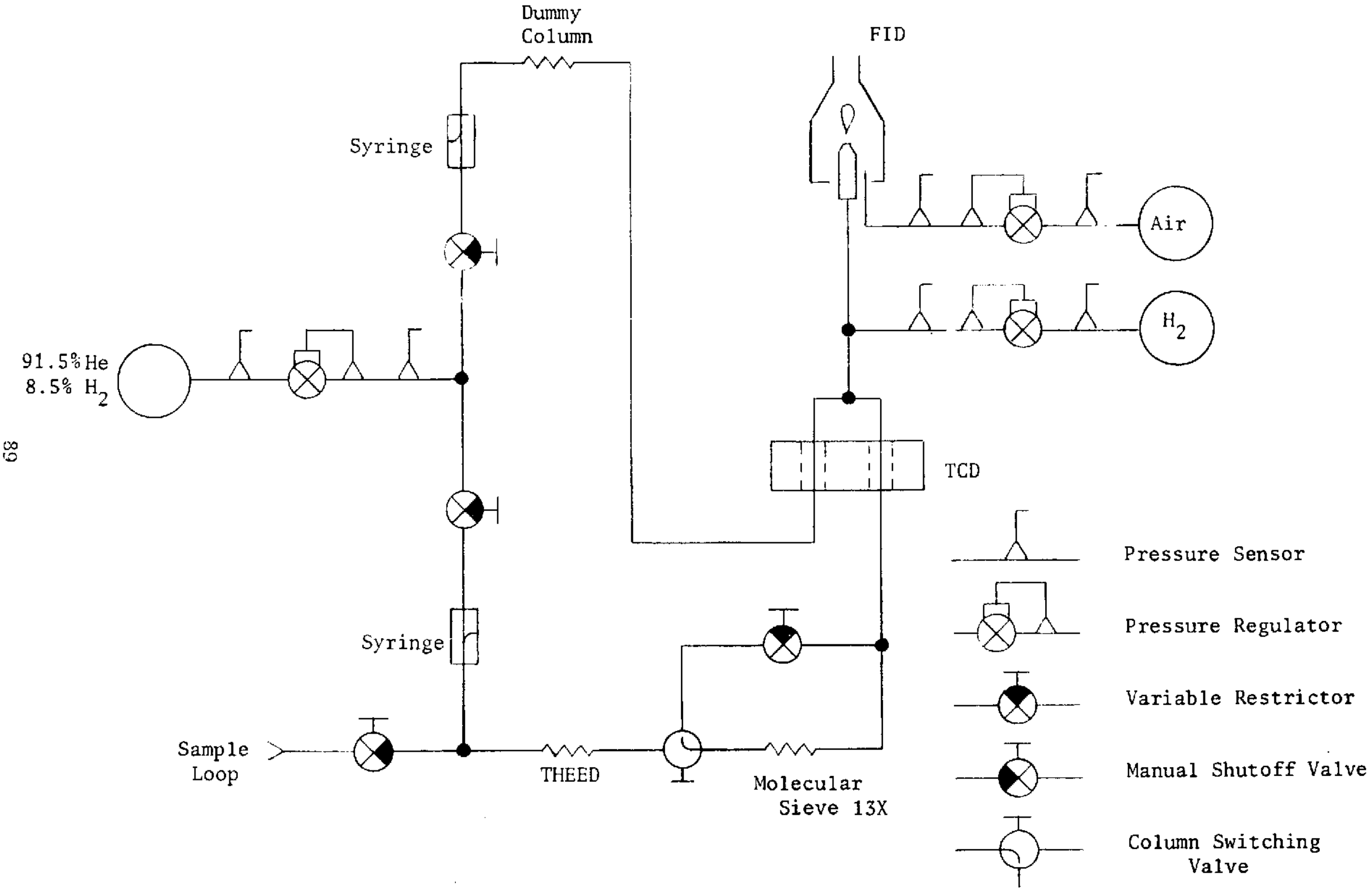


FIGURE 42 SCHEMATIC OF CARLE AGC-311 WITH SAMPLE VALVE AND COLUMN SWITCHING VALVE

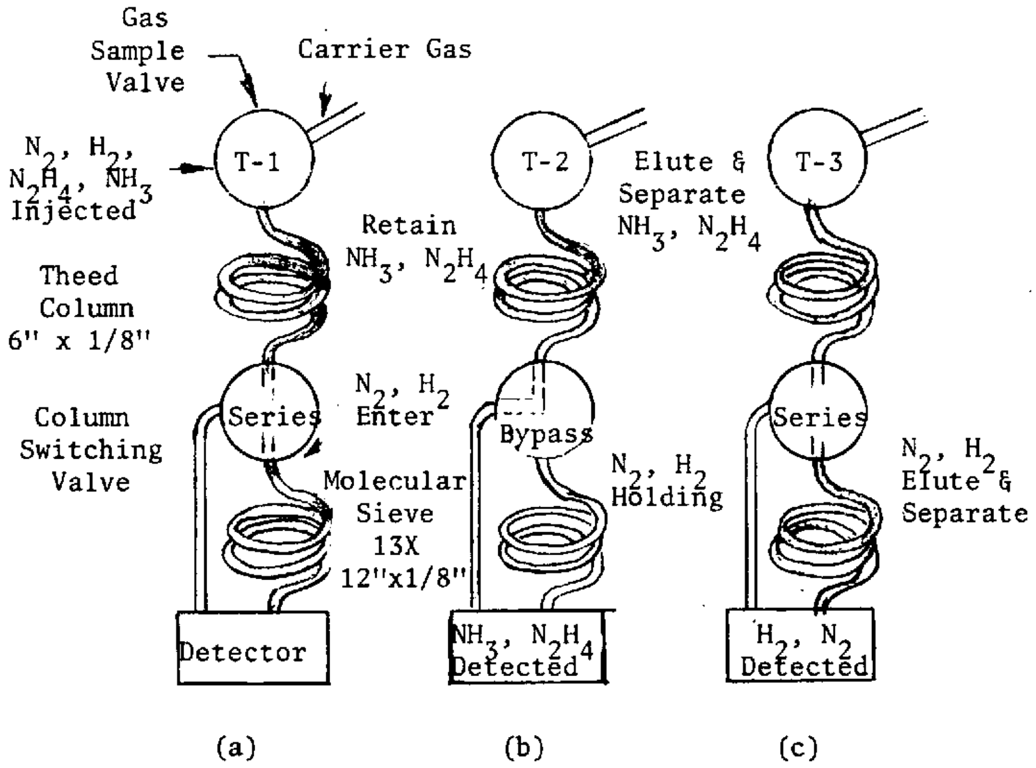
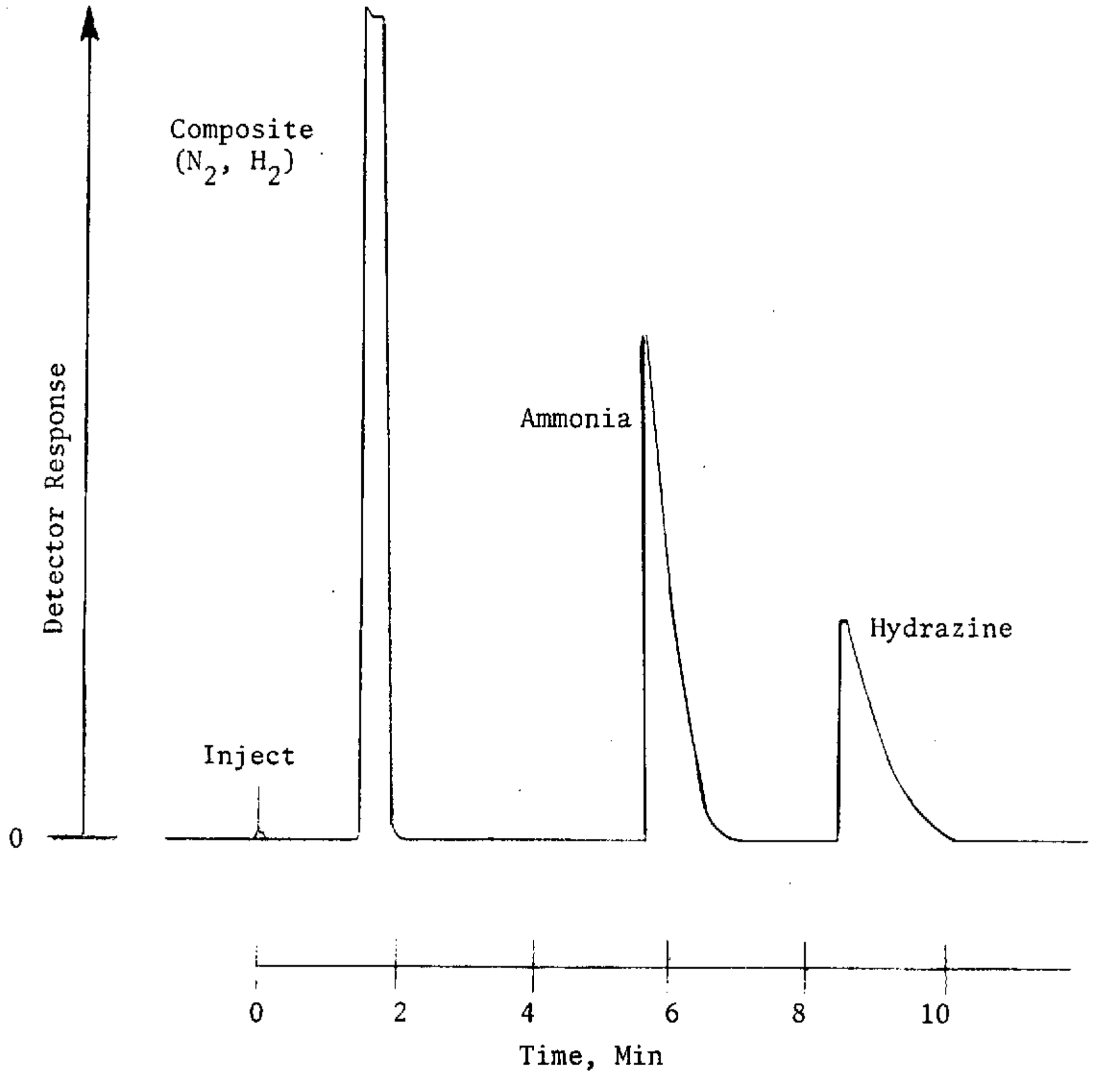


FIGURE 43 SERIES BYPASS SWITCHING GAS CHROMATOGRAPH OPERATION SCHEMATIC

C-2



Column

6 Ft x 1/8 In Teflon,
packed with 4% THEED
on 40-80 mesh Graphon

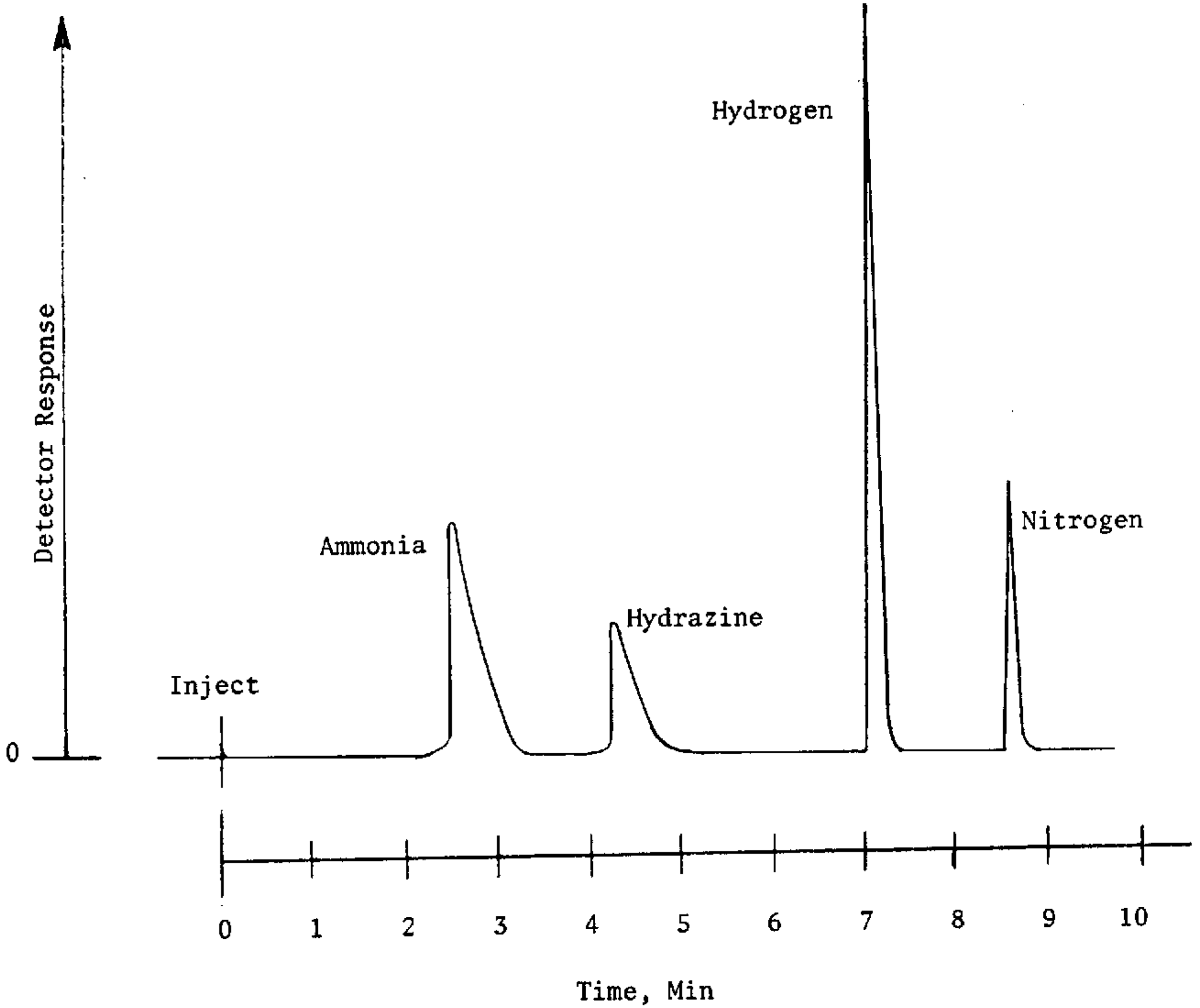
Carrier

91.5% He
8.5% H_2
@ 25 ml/min

Sample Size

1 cc Sample Mixture

FIGURE 44 CHROMATOGRAM WITH COMPOSITE N_2, H_2 PEAK



Column 1

6 Ft x 1/8 In Teflon,
packed with 4% THEED
on 40-80 mesh Graphon

Column 2

12 Ft x 1/8 In
Molecular Sieve 13X

Carrier

91.5% He
8.5% H_2
@ 25 ml/min

Sample Size

1 cc Mixture

FIGURE 45 CHROMATOGRAM WITH RESOLVED N_2, H_2 PEAKS

Programmed Temperature Gas Chromatography (Varian 1720-10)

The technique of programmed temperature gas chromatography is a logical extension of the isothermal method and was developed for the analysis of multicomponent mixtures. The technique is well-suited for the present application where the constituents show widely different affinities for the adsorbent as a function of temperature.

In programmmed temperature gas chromatography, the temperature of the entire column is increased with time. There is no variation in the temperature along the column. In order to effect programmed temperature gas chromatography using thermal conductivity detectors, several requirements must be met. The programmed temperature technique requires a column temperature separately controlled from the detector. It is desirable that the detector block be maintained at a high constant temperature and not be affected by column temperature changes. Carrier gas at constant pressure must be maintained at a constant flow rate by a flow controller, even though the resistance to flow in the column changes (increases with increasing in column temperature). Further, it is necessary to maintain a constant pressure on the reference and detector side.

A 1.2 - 1.8 m (4 - 6 ft) molecular sieve 5a or 13X is used to separate and quantitatively analyze the multicomponent gas samples containing N_2, H_2, NH_3, and N_2H_4. The column temperature is programmed at 0.10 - 0.15 K/s^2 (10.8 - 16.2 F/min) from 293 to 573K (68 to 572F).

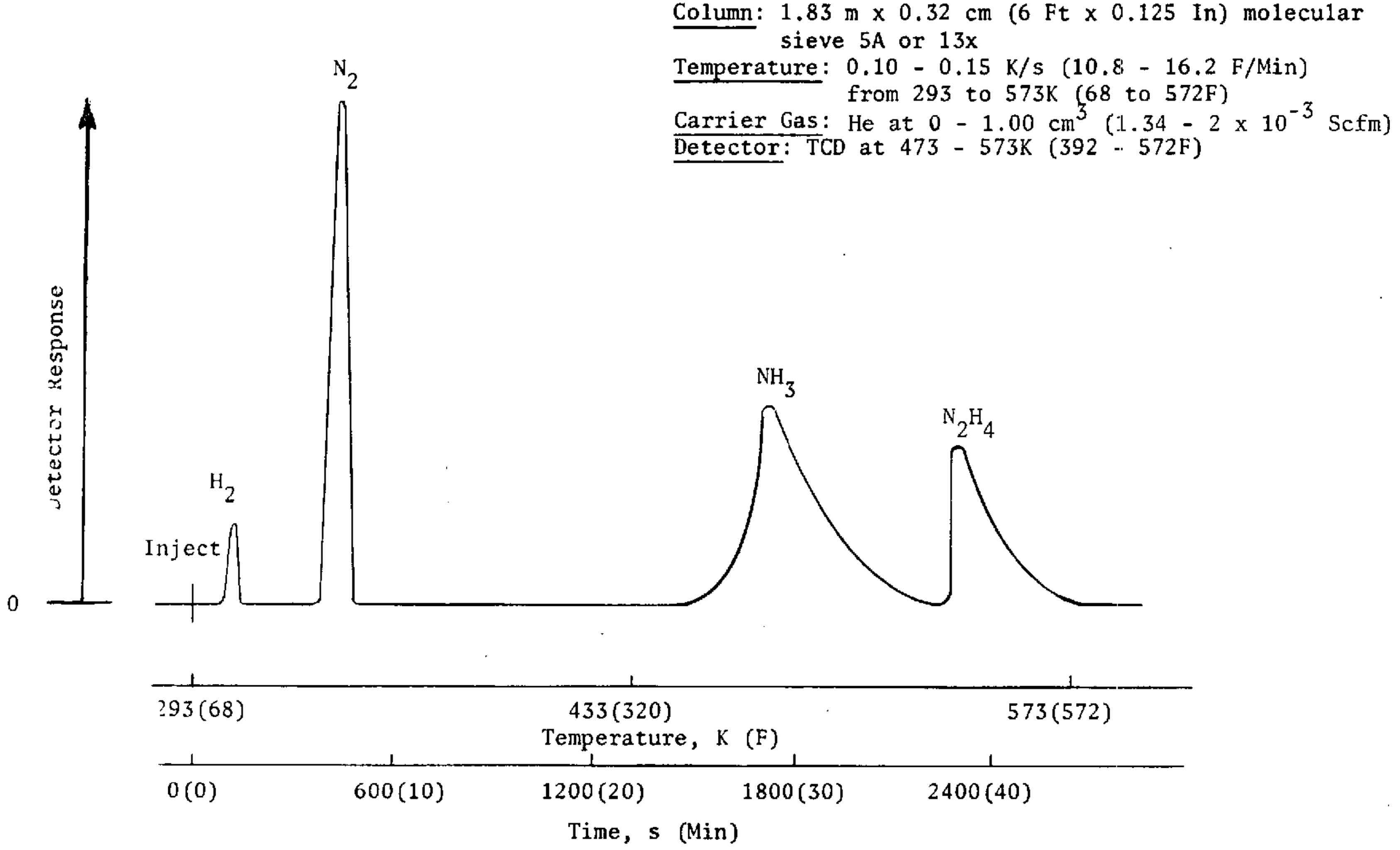
A typical chromatogram that will result from such an analysis is shown in Figure 46.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions are a direct result of this development:

1. A two-stage Pd/Ag N_2/H_2 Separator was demonstrated to be a simple and effective method of N_2/H_2 separation for the application. The two-stage Pd/Ag N_2/H_2 Separator developed is capable of delivering 6.81 kg/d (15 lb/day) of 99.1% to 99.9% (by volume) pure N_2 at 1691 kN/m^2 (245 psia) and 0.83 kg/d (1.82 lb/day) of ultrapure (greater than 99.9999% by volume) H_2 at 172 kN/m^2 (25 psia). The remaining H_2 by-product is removed to vacuum in the Pd/Ag second stage to achieve the desired N_2 purity. As a result, approximately 0.15 kg/d (0.32 lb/day) of H_2 would not be available for spacecraft usage. The Pd/Ag diffusion tubes are compatible with NH_3 and present Pd/Ag technology is adequate for developing hardware for the application.

2. A Polymer Diffusion Unit and an Electrochemical N_2/H_2 Separator can be effectively integrated to perform the N_2/H_2 separation process. The Polymer-Electrochemical N_2/H_2 Separator developed is capable of delivering 6.81 kg/d (15 lb/day) of 99.6% to 99.9% (by volume) pure N_2 at 1035 kN/m^2 (150 psia) and 0.98 kg/d (2.14 lb/day) of 97.5% to 98.7%



<u>Column</u>: 1.83 m x 0.32 cm (6 Ft x 0.125 In) molecular sieve 5A or 13x
<u>Temperature</u>: 0.10 - 0.15 K/s (10.8 - 16.2 F/Min) from 293 to 573K (68 to 572F)
<u>Carrier Gas</u>: He at 0 - 1.00 cm^3 ($1.34 - 2 \times 10^{-3}$ Scfm)
<u>Detector</u>: TCD at 473 - 573K (392 - 572F)

FIGURE 46 LINEAR PROGRAMMED TEMPERATURE CHROMATOGRAM FOR N_2, H_2, NH_3, AND N_2H_4 GAS MIXTURE ANALYSIS

(by volume) pure H_2 at 172 kN/m^2 (25 psia). The separation process is a low power consumption process with the Electrochemical N_2/H_2 Separator module requiring only 25 watts of power. The incompatibility of the polymer material to the NH_3 concentration in the N_2H_4 Catalytic Dissociator product gas stream, however, eliminates the present polymer diffusion design from being used for the application. An advanced Polymer Diffusion Unit design having a compatible polymer membrane material is within the state-of-the-art but would have to be developed prior to integration with the N_2H_4 Catalytic Dissociator.

3. A N_2H_4 Catalytic Dissociator is capable of dissociating 7.78 kg/d (17.14 lb/day) of liquid N_2H_4 (5.4 cm^3/min) to yield sufficient N_2 for the application. The important performance criteria, however, is to minimize the NH_3 concentration in the product gas stream. A modification to the present N_2H_4 Catalytic Dissociator design is required to lower the NH_3 concentration in product gas stream from 2.5% to 0.5% (by volume) and to retain the polymer-electrochemical approach as a viable option in spacecraft N_2 generation.

4. Control and monitor instrumentation for N_2 Generation System applications can be developed to provide for fully automatic, fail-safe N_2 Generation System operation as demonstrated by the instrumentation hardware integrated with the Polymer-Electrochemical N_2/H_2 Separator.

The following recommendations are a direct result of the program's conclusions:

1. The next step in developing a N_2 Generation System should be integrating the N_2H_4 Catalytic Dissociator and the two-stage Pd/Ag N_2/H_2 Separator and endurance testing the system for 60 days.

2. Further development of the integrated Polymer-Electrochemical N_2/H_2 Separator and N_2H_4 Catalytic Dissociator should be delayed pending the development of the improved polymer material. A compatible membrane will evolve industrially in approximately two to five years without NASA support. As a first step in support of this development, it is recommended that a sample of the new membrane material be obtained and tested for compatibility with ammonia concentrations of 2.5%.

3. Improved N_2H_4 Catalytic Dissociator performance should be investigated in the areas of catalyst selection, loading, and bed length. Modifications to the design should be incorporated and the performance improvement demonstrated prior to and upon integration with the Pd/Ag N_2/H_2 Separator.

REFERENCES

1. Marshall, R. D., Wynveen, R. A., and Carlson, J. N., "Evaluation of an Electrochemical N_2/H_2 Gas Separator," Final Report, LSI ER-168-8, NASA CR-114580, Life Systems, Inc., Cleveland, Ohio, March, 1973.

2. Marshall, R. D., "Spacecraft Nitrogen Resupply Technology: Nitrogen/Hydrogen Separation," 74-ENAs-9, presented at the Intersociety Conference on Environmental Systems, Seattle, Washington, July 29-August 1, 1974.

3. Personal telephone communications with Mr. J. F. Hannan at E. I. Dupont.

4. Audrietti, L. F., and Ogg, B., "The Chemistry of Hydrazine," J. Wiley and Sons, Inc., New York, New York, 1951.

5. Smetana, Frederick O., Fairchild II, Howard N., and Martin, Glenn L., "Equilibrium Concentrations of N_2H_4 and its Decomposition Products at Elevated Temperatures and Pressures," Department of Mechanical and Aerospace Engineering, School of Engineering, North Carolina State University, Raleigh, North Carolina.

6. Ciprios, George, "Multiple Reserve Electrochemical Power Source," Esso Research and Engineering Company, Linden, New Jersey, Energy 70 Proceedings, Fifth Intersociety Energy Conversion Engineering Conference, Vol. 1.

7. Telecon with Haldor-Topsoe representative in Houston, Mr. Erik Vohtz.

APPENDIX 1 MODE TRANSITION SEQUENCES

POWER ON

When the control instrumentation circuit breakers are manually closed the Power-On-Reset (POR) circuit in the system causes the sequence logic to go to the STOP mode. The system is then ready for a START command.

START SEQUENCE

1. Operate the START/OVERRIDE pushbutton. The green START light will illuminate. (Note that if the amber OVERRIDE half of the START/OVERRIDE switch is illuminated it indicates that one or more of the OVERRIDE switches on the back panel of the control instrumentation package is not in the automatic position. This will not prevent the system from progressing through the startup sequence. It will, however, prevent operation of the controlled items whose switches are not in the automatic position.
2. Coolant pump on.
3. WATER FILL sequence initiated (see Water Tank Fill Sequence below).
4. WATER FILL sequence completed.
5. PURGE sequence initiated (see Purge Sequence below).
6. PURGE sequence completed.
7. Solenoid valve SV1 energized.
8. When the N_2 out flow reaches a preset minimum value, Stage 2 and 3 currents are enabled. Solenoid valves SV4 and 5 are now controlled by Stage 3 as described in the VENT sequence "C."

VENT SEQUENCE

1. In NORMAL operating mode (at end of Start Sequence) and Stage 3 changes from NORMAL constant voltage mode (i.e., low H_2 content in N_2 from system) to a constant current mode (i.e., high H_2 content in N_2 from system), initiate VENT sequence.
2. Deenergize SV4, SV5, and start vent timer. This is VENT mode and the sequencer will stay in this mode until either (a) Stage 3 returns to voltage control mode at which time SV4 and SV5 will become energized and the VENT timer reset, or (b) the VENT timer completes its time period which sends the system into a SHUTDOWN sequence (see Shutdown Sequence below).

WATER FILL SEQUENCE

1. A water tank fill cycle is initiated by a timer (approximately every 24 hours) or whenever the system changes from STOP mode to a startup sequence.
2. Solenoid valve SV9 energized, isolating the water tank from the module.
3. Solenoid valve SV10 energized, which allows the pressure in the H_2 side of the water tank to bleed slowly through a restrictor.
4. Wait for two minute delay to allow bleeding to occur.
5. Solenoid valve SV11 energized, which allows the water in to refill the water accumulator tank.
6. When the water tank becomes full, a change in pressure will be indicated by the pressure switch PS2.
7. Solenoid valve SV11 deenergized, which stops the water filling the tank.
8. Solenoid valve SV10 deenergized. This allows the H_2 side of the water tank to slowly repressurize through the restrictor.
9. Wait for two minute delay to allow for this repressurization.
10. Solenoid valve SV9 deenergized. This allows water to flow to the module.
11. Twenty-four hour timer allowed to start timing again.

PURGE SEQUENCE

1. A PURGE sequence is initiated in either a startup or shutdown sequence to purge the system with N_2.
2. Solenoid valves SV2, 3, 6, and 7 energized.
3. Wait two mintues for N_2 to purge system.
4. Solenoid valves SV 2, 3, 6, and 7 deenergized.
5. Continue on with startup or shutdown sequence as required.

SHUTDOWN SEQUENCE

1. A shutdown sequence can be initiated in three ways: (1) by operating the STOP pushbutton, (2) by a malfunction shutdown signal received

from the monitoring instrumentation package, or (3) by the vent timer when it times out (see Vent Sequence above).

2. If a fill cycle is in progress it will be allowed to be completed.
3. If the system is not in a fill cycle when the shutdown is initiated, solenoid valve SV1 is deenergized, current to Stages 2 and 3 is disabled, and the fill cycle timer is disabled.
4. Coolant pump off.
5. Solenoid valves SV7 and SV8 energized to vent system.
6. Wait two minutes for vent to occur.
7. PURGE sequence initiated (see Purge Sequence above).
8. PURGE sequence completed.
9. Deenergize solenoid valves SV2, SV3, SV6, SV7, and SV8. The system is now in the STOP mode.