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Frank W. Gilleland

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ABSTRACT

The electrical output and the mechanical condition of silicon solar cells with titanium silver grids and contacts has been studied in atmospheres which could be created by proposed spacecraft attitude control systems. The effects on silicon solar cells of atmospheres of ammonium hydrogen sulfide at temperatures ranging from -20°C to +20°C and atmospheres of Freon 14 gas have been investigated. Experimental results indicate that no short-term degradation of solar arrays which use silicon cells with titanium silver grids and contacts is to be anticipated as a result of exposure to these gases.

SUMMARY

Two attitude control systems (ACS) have been proposed for use on the AIMP-E spacecraft, one uses ammonium hydrogen sulfide as a subliming fuel and the other uses Freon 14 gas. It is anticipated that as a result of using either of these systems the spacecraft could be enveloped in a cloud of ammonia (NH_3) and hydrogen sulfide (H_2S) or Freon 14 with a pressure of about 10^{-5} Torr.

To determine the effects of ammonia and hydrogen sulfide gases on the solar paddles, four modules of silicon solar cells with titanium silver grids and contacts were exposed to the gases at temperatures ranging from -20°C to +20°C. This was done at pressures from two (2) Torr to fifty (50) Torr. The electrical output and the mechanical condition of the solar cells were monitored throughout the investigation. A literature survey was conducted regarding the effects of Freon 14 gas on the solar cells.

The results of this investigation indicate that no short term degradation of the solar paddles on the AIMP-E Spacecraft is to be anticipated as a result of the use of either of the proposed attitude control systems.

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INTRODUCTION

The first Anchored Interplanetary Monitoring Platform (AIMP-D, Explorer XXXIII) was launched on 1 July 1966 into an alternate mission which was a highly eccentric earth orbit. Post-launch investigation revealed that the primary mission, a lunar orbit, could have been achieved had the spacecraft incorporated a small rocket system which could have changed the attitude of the spacecraft just prior to firing the fourth stage rocket motor and injection into orbit. To this end two attitude control systems (ACS) were proposed for use on the second Anchored Interplanetary Monitoring Platform (AIMP-E, Explorer XXXV) to be launched in July 1967.

The first, and theoretically more effective system, employed ammonium hydrogen sulfide (NH_4HS) as a subliming fuel. The ammonium hydrogen sulfide crystals were stored in a small container under low pressure. Upon being opened to the vacuum of space the crystals sublimed forming both ammonia (NH_3) and hydrogen sulfide (H_2S) gases. These gases were then released through small jets or nozzles mounted at the tips of two of the spacecraft's four solar paddles.

The second attitude control system which was proposed utilized Freon 14 gas stored in a small container under relatively high pressure and again released through the small nozzles on the tips of the solar paddles.

Since it was common knowledge that silver tarnishes in the presence of sulphur — even in the amounts present in the ordinary atmosphere, questions were raised as to the stability of the titanium silver solar cell contacts under exposure to the hydrogen sulfide gas. Specifically, solar cells in covered, but unsealed, packing boxes had shown serious contact discoloration when "on the shelf" for one year's time and the questions raised were:

(1) How significant is the effect from the standpoint of electrical stability?

(2) How significant is the effect under expected flight conditions?

(3) Are there any other effects under expected flight conditions, and how significant are they?

These questions, concerning the effect of ammonium hydrogen sulfide on the power output of the solar paddles, became particularly serious when a few samples of silicon solar cells with titanium silver grids and contacts were subjected to a considerable dosage of the gas during an initial compatibility test. The mechanical damage incurred by the test samples was so serious that post-test electrical evaluation was impossible. The silver on the solar cells had turned black and had delaminated.

It was realized that under most conditions hydrogen sulfide will react with silver to form the black colored compound silver sulfide. This was apparently what had occurred during the initial compatibility tests. It was also apparent that the physical location of the exhaust nozzles at the ends of the solar paddles was such that the solar paddles would be partially engulfed by the plume of exhaust gases from the attitude control system. Further, it was believed that the entire spacecraft would possibly be enveloped in a cloud of ammonia and hydrogen sulfide or a cloud of Freon 14, depending upon which attitude control system was used, with a pressure of about 10^{-5} Torr.

Thus the investigation undertaken in this project was to determine the degradation of mechanical and electrical properties of silicon solar cells with titanium silver grids and contacts in an atmosphere of ammonium hydrogen sulfide and also in an atmosphere of Freon 14 gas.

EXPERIMENT

Approach

Silicon solar cells with titanium silver grids and contacts were placed in a vacuum chamber (Figures 1 and 2) where both the temperature and atmosphere could readily be controlled. The cells were then subjected to various temperatures from -20°C to +20°C and to various atmospheres of ammonia and hydrogen sulfide at pressures from 2 Torr to 50 Torr. During these tests the electrical output of the cells under tungsten-iodide light was monitored by recording Current-voltage (I-V) curves (See Figure 3, for example) for each of the test modules.

The effects of Freon 14 gas on the silicon solar cells with titanium silver contacts was investigated through a literature survey which indicated no laboratory investigation was warranted.

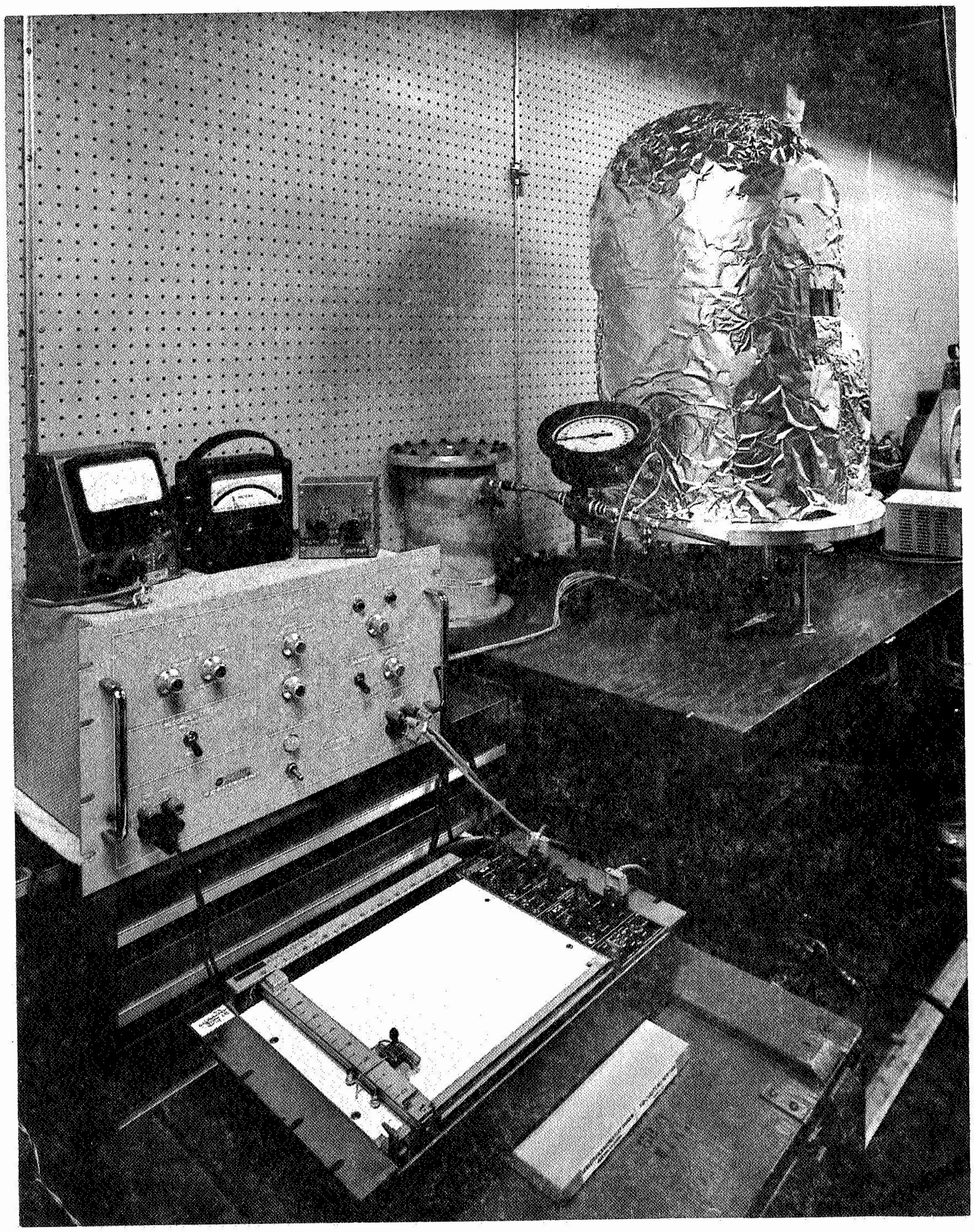

Figure 1. Test Equipment

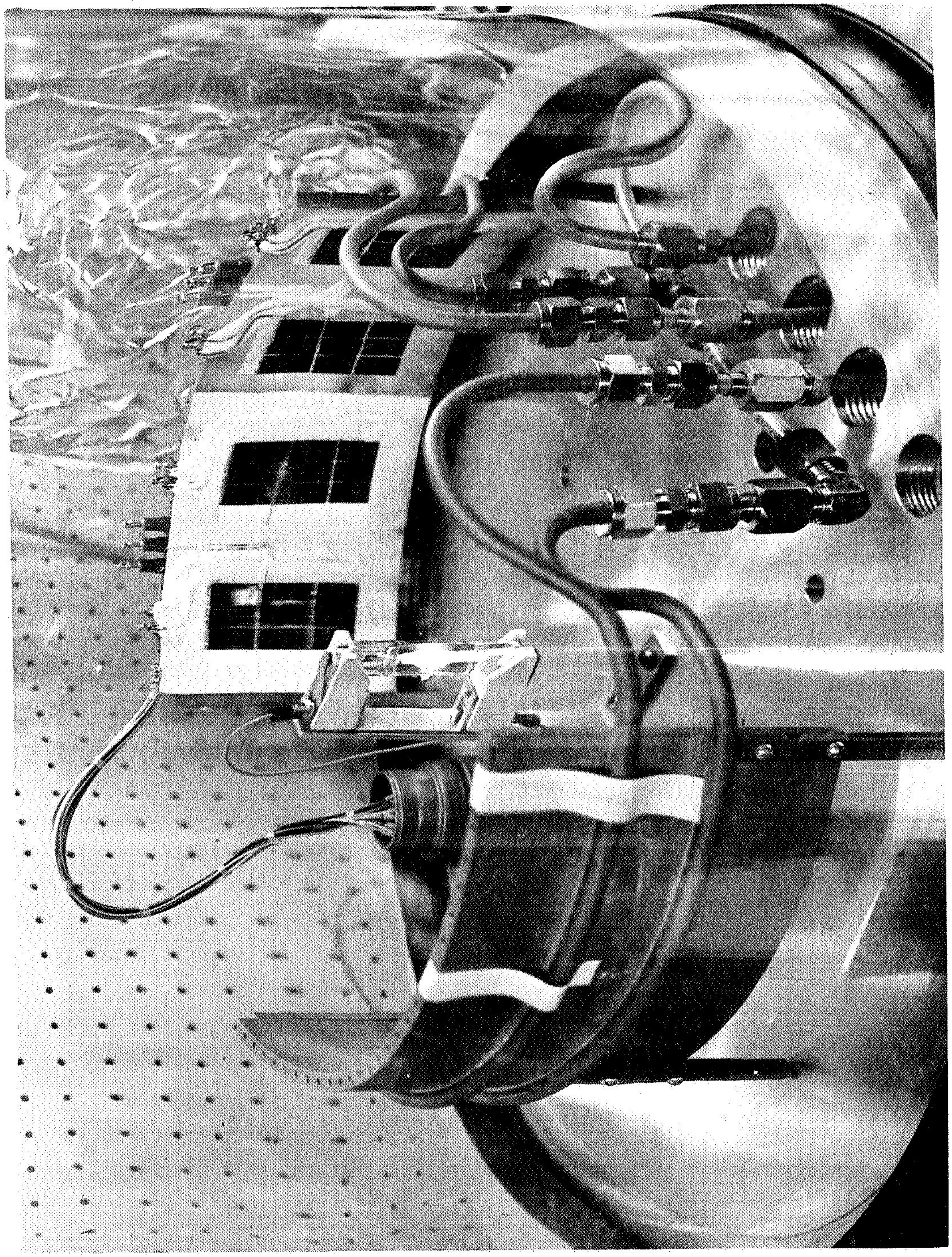

Figure 2. Test Chamber

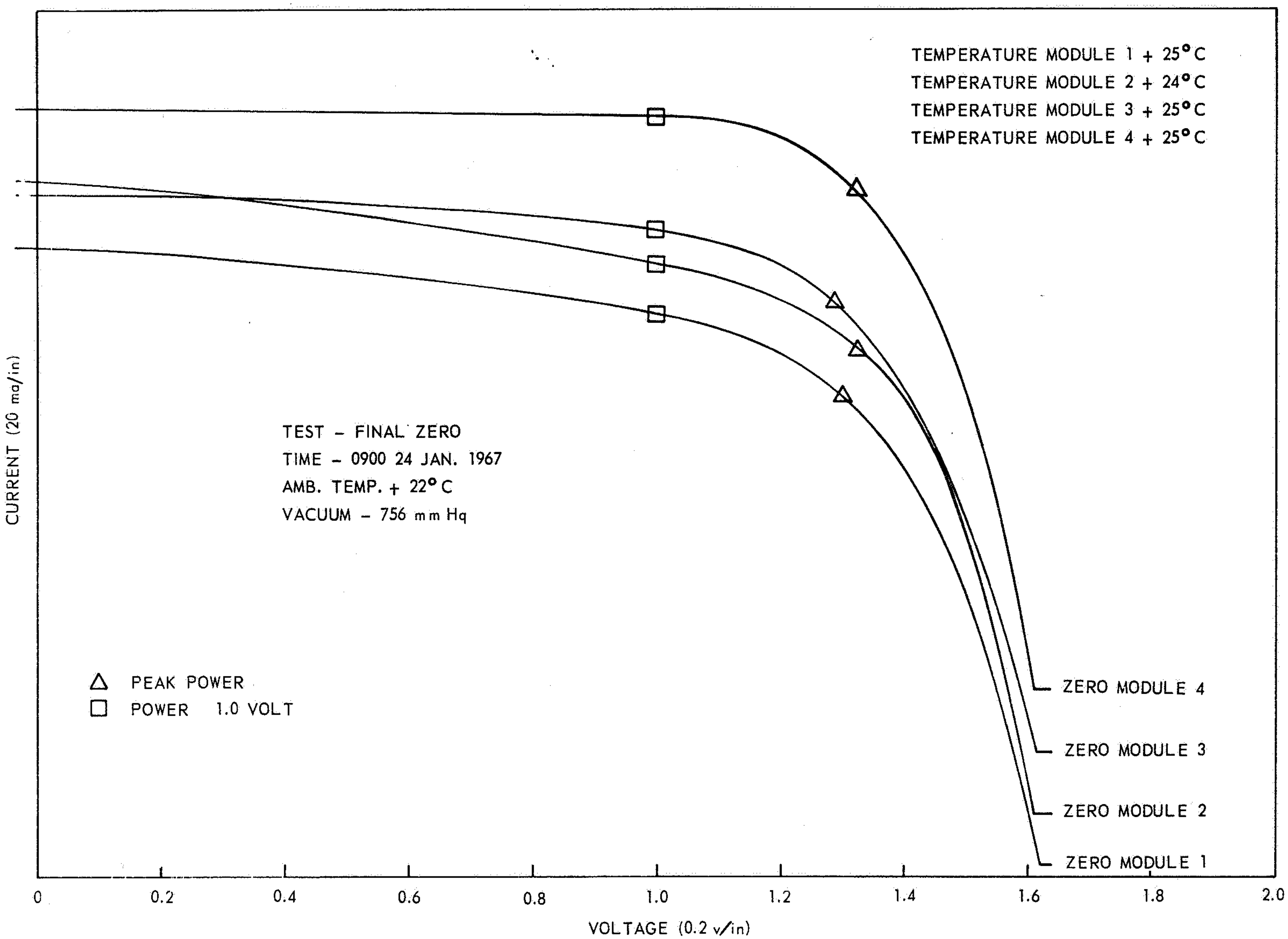

Figure 3. Sample Current Voltage Curves

Procedure

Three separate tests were conducted, numbered one through three, each holding the modules at a constant temperature of 20°C, 0°C and -20°C respectively. These values for temperature were selected because it was calculated that the solar paddles of the AIMP-E spacecraft would operate primarily within this range.

The following procedure was used for each of the three tests:

1. The test chamber was evacuated and the temperature of the four modules allowed to stabilize at the desired value. At this time the lamp was turned on and I-V curves were recorded for each of the four modules. The lamp was on for a minimum amount of time to avoid unnecessary heating of the environment. This I-V curve was referred to as the "zero" curve and all further evaluation parameters in the test were normalized to it.

2. Ammonium hydrogen sulfide was allowed to enter the test chamber as rapidly as was possible until the pressure had increased 50 Torr for Test #1, 10 Torr for Test #2 and 2 Torr for Test #3. These values of pressure were chosen to preclude the condensing of the gases on the test chamber surfaces. Again I-V curves were recorded as previously described for each of the four modules.

3. As soon as was possible the test chamber was evacuated and for a period of about one hour and fifteen minutes after the ammonium hydrogen sulfide had been admitted to the chamber I-V curves were taken at convenient intervals.

At the conclusion of the three tests, conducted at their respective temperatures and pressures, the modules were permitted to return to room temperature where they remained overnight in vacuum. The following morning I-V curves were recorded for each module at room temperature.

Equipment

The test equipment which was used in this investigation is shown in Figures 1 and 2. It consists basically of a large vacuum chamber in which a controlled amount of ammonium hydrogen sulfide gas could be injected. The gas could be cleared from the chamber by exhausting it to the outside of the building through a conventional vacuum pump. (Safety requires that exhausting be done <u>outside</u> the building. See appendix A.)

All of the solar cells used were 1 cm × 2 cm, N/P, blue shifted silicon solar cells with titanium silver grids and contacts. The test cells shown in Figure 2, consisted of four modules, with each module consisting of three cells in series and three cells in parallel. Two of the modules had fused silica cover slides bonded to each individual cell with General Electric RTV-602, the other two modules had bare cells. The modules were assembled with silver expanded metal interconnectors and were bonded to an electrical insulating layer of resin impregnated fiber glass cloth (Micaply) with General Electric RTV-40. The fiber glass cloth was in turn bonded with RTV-40 to the substrate which was 0.25 in. thick stainless steel, 4 in. high and curved to a radius of 7 in. All of the electrical wiring used within the chamber was insulated with irradiated polyolefin.

The temperature of each individual module was monitored through the use of a thermistor bonded to the front of each module. The temperature of the modules was controlled to the desired temperature by passing liquid nitrogen through one quarter inch diameter coils welded on the back of the stainless steel substrate.

The light source used for the investigation was a 600 watt tungsten-iodide (Sylvania Sun Gun) bulb. It was positioned symmetrically in the center of the test chamber at the center of curvature (a distance of seven inches from each test module) of the substrate. The intensity of the lamp was controlled using a variable voltage power source. Prior investigation of the light source showed the ability to reproduce the same intensity of illumination after turning the lamp off and on again was within plus or minus three per-cent.

Recording instruments consisted of an electronic load read out on an X-Y plotter. A switch permitted obtaining complete I-V curves for each of the four modules in less than forty-five seconds.

Tolerance on Experimental Values

Considerable difficulty was experienced in holding the module temperatures constant. When the light source was turned on the module temperatures rose very rapidly making it very difficult to determine accurately the N/P junction temperature; thus it was felt that the accuracy with which the N/P junction temperature was known was ±10°C. Past experience at Goddard Space Flight Center indicates that this would cause a ±1% variation in the short circuit current and a ±4.5% variation in open circuit voltage.

The reproducibility of the light source was demonstrated to be within ±3% due to line voltage variations and temperature variations.

The reliability of the electronic load was ±1% and that of the X-Y plotter ±1/2% based upon manufacturers data.

A statistical average of these terms would result in an error of:

1. For short circuit current:

$$\text{Error} = [0.5\%^2 + 3\%^2 + 1\%^2 + 1\%^2]^{1/2}$$

$$\text{Error} = 3.4\%$$

2. For open circuit voltage:

$$\text{Error} = [0.5\%^2 + 3\%^2 + 1\%^2 + 4.5\%^2]^{1/2}$$

$$\text{Error} = 5.9\%$$

Errors for the power at one volt and peak power would fall somewhere in between the errors for the short circuit current and the open circuit voltage.

DISCUSSION OF RESULTS

Ammonium Hydrogen Sulfide Exposure Results

The data obtained from the test measurements was evaluated by analyzing a number of individual electrical parameters, i.e. short circuit current (I_{sc}), open circuit voltage (V_{oc}), peak power (P_P) and power at 1.0 volt (P_1). The values for these specific points were obtained from the raw data (I-V curves) and then normalized against the initial reading taken before the introduction of the ammonium hydrogen sulfide gas to the test chamber. These normalized values have been plotted in Figures 4-9.

The experimental error was calculated to be ±3.4% to ±5.9% depending upon the particular parameter under consideration. All data was within the anticipated error with one exception. Two data points warrant further consideration.

In test No. 1 it was apparent that the light intensity increased during the last three readings. This was indicated because the power at the maximum power point, the power at 1.0 volt and the short circuit current all increased beyond previous experimental values, yet the open circuit voltage remained the same indicating no significant change in temperature. Had there been a decrease in

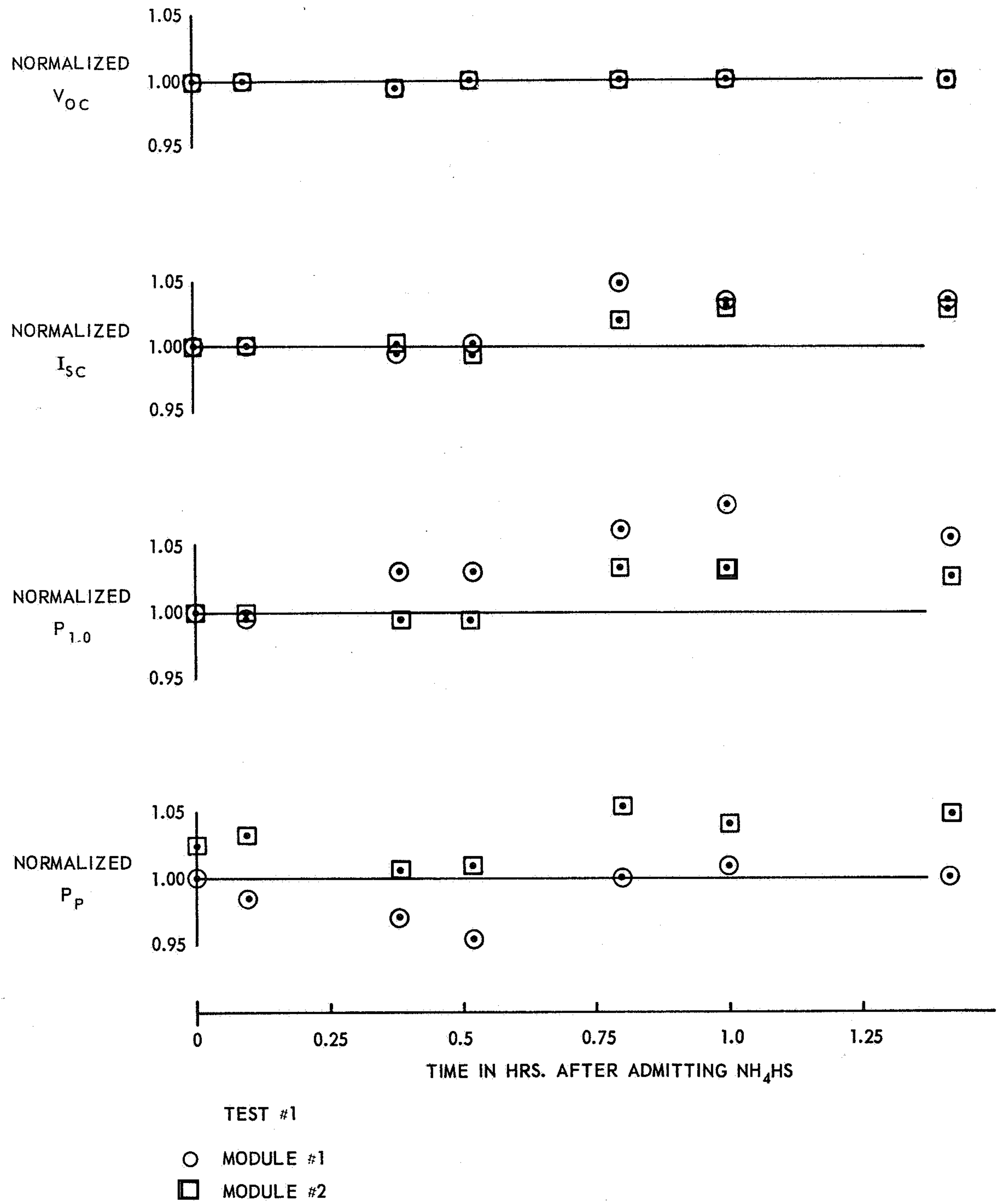

Figure 4. Normalized Electrical Parameters vs. Time for Modules Without Coverslides at 20° C

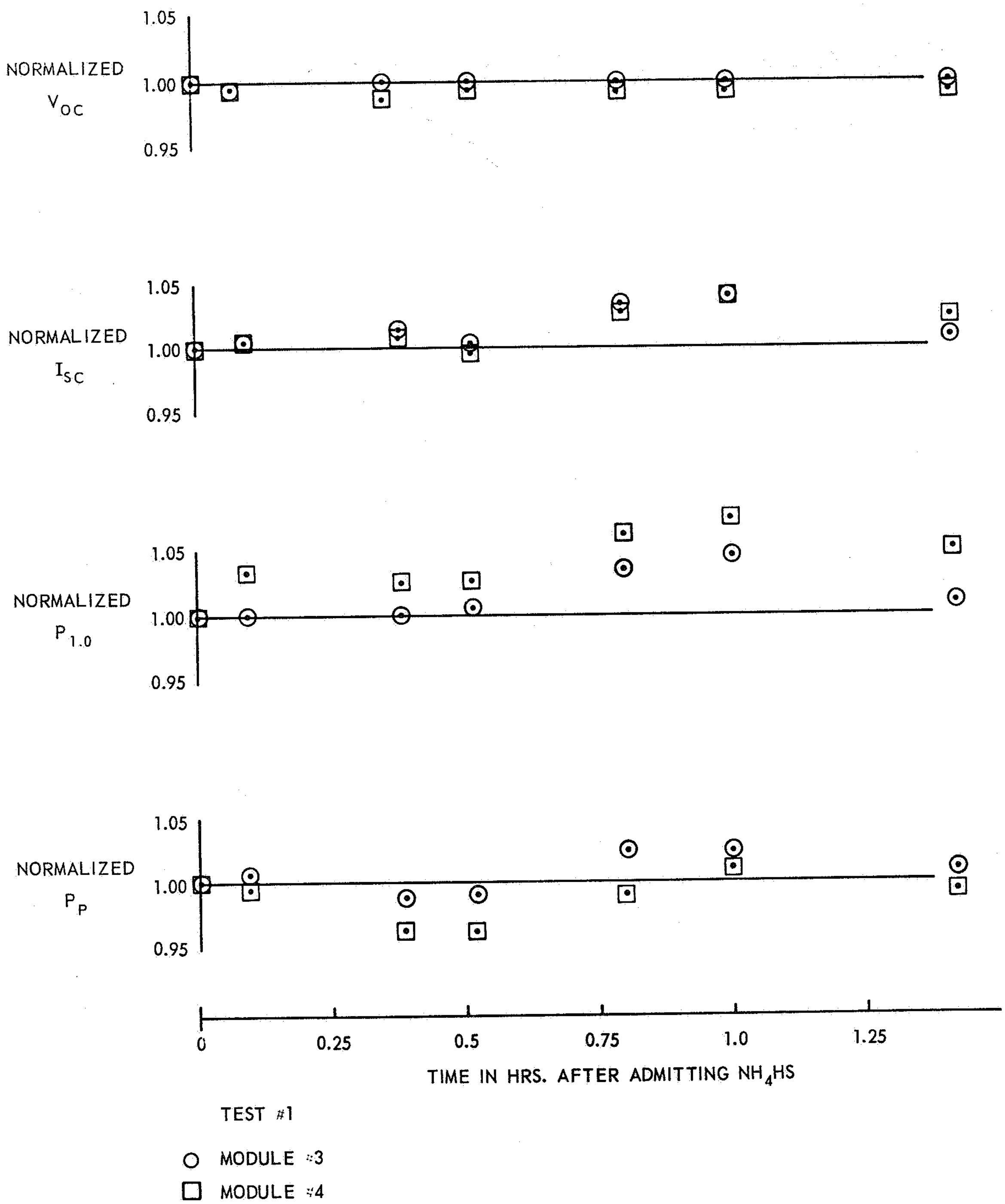

Figure 5. Normalized Electrical Parameters vs. Time for Modules With Coverslides at 20° C

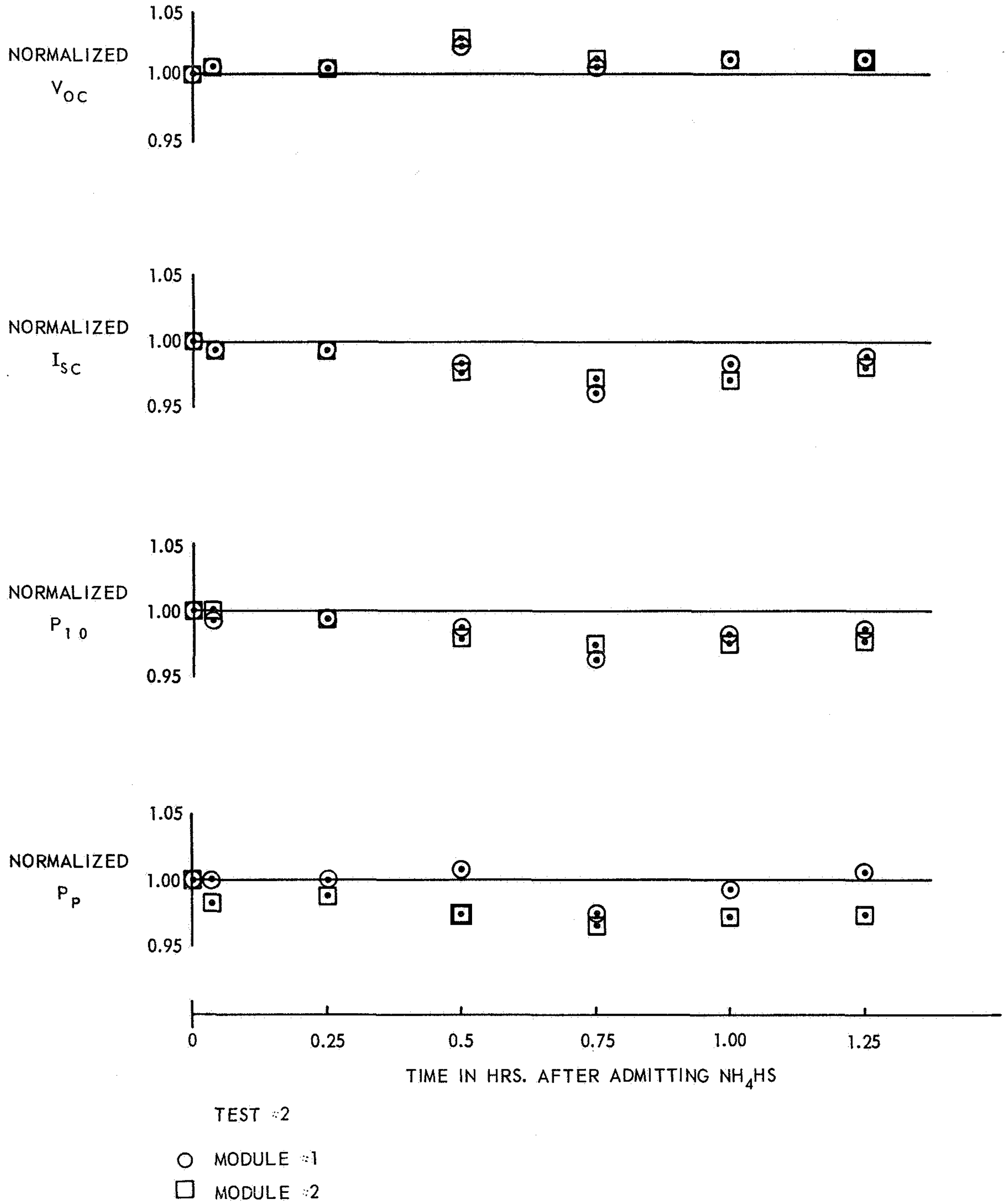

Figure 6. Normalized Electrical Parameters vs. Time for Modules Without Coverslides at 0° C

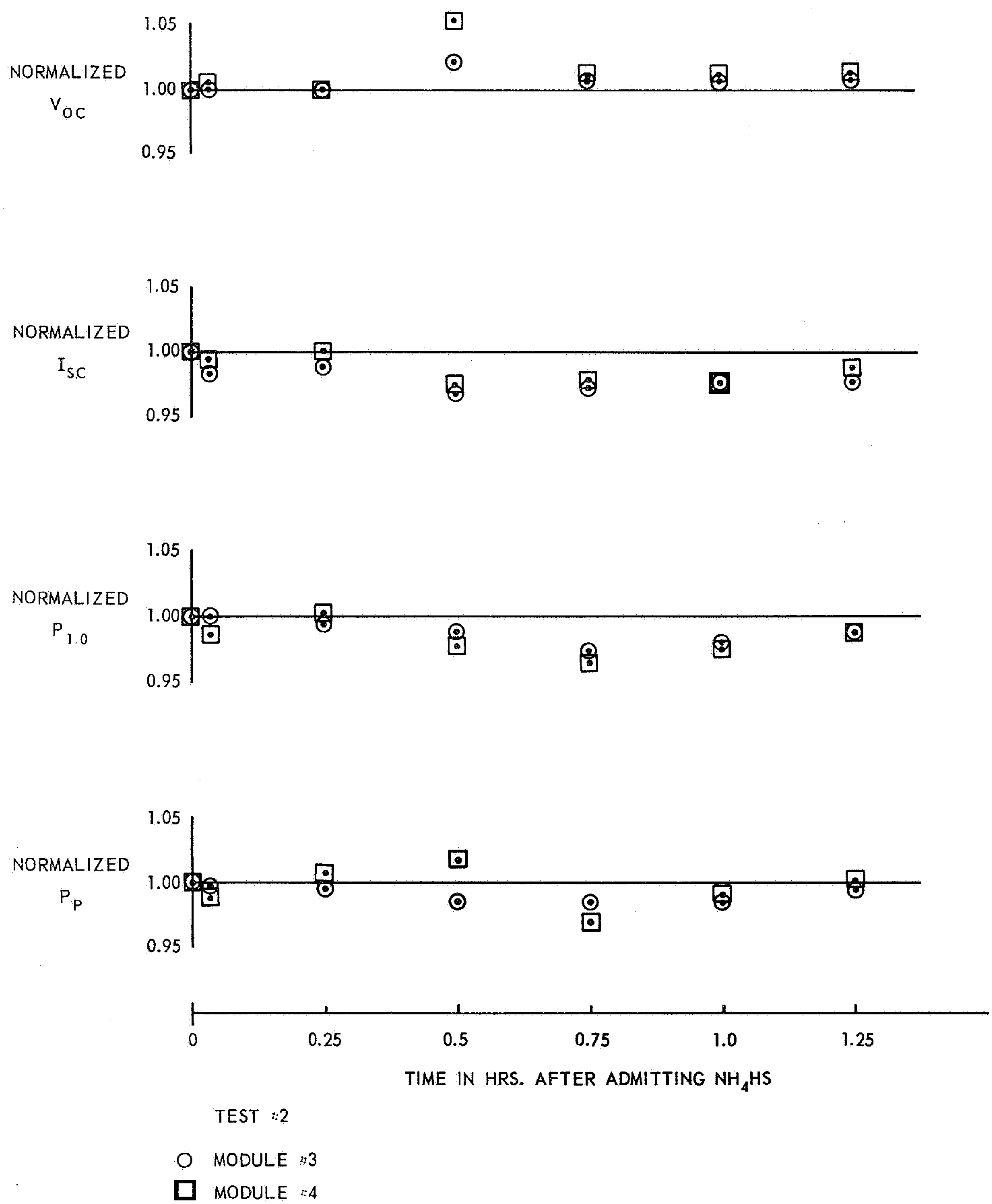

Figure 7. Normalized Electrical Parameters vs. Time for Modules With Coverslides at 0° C

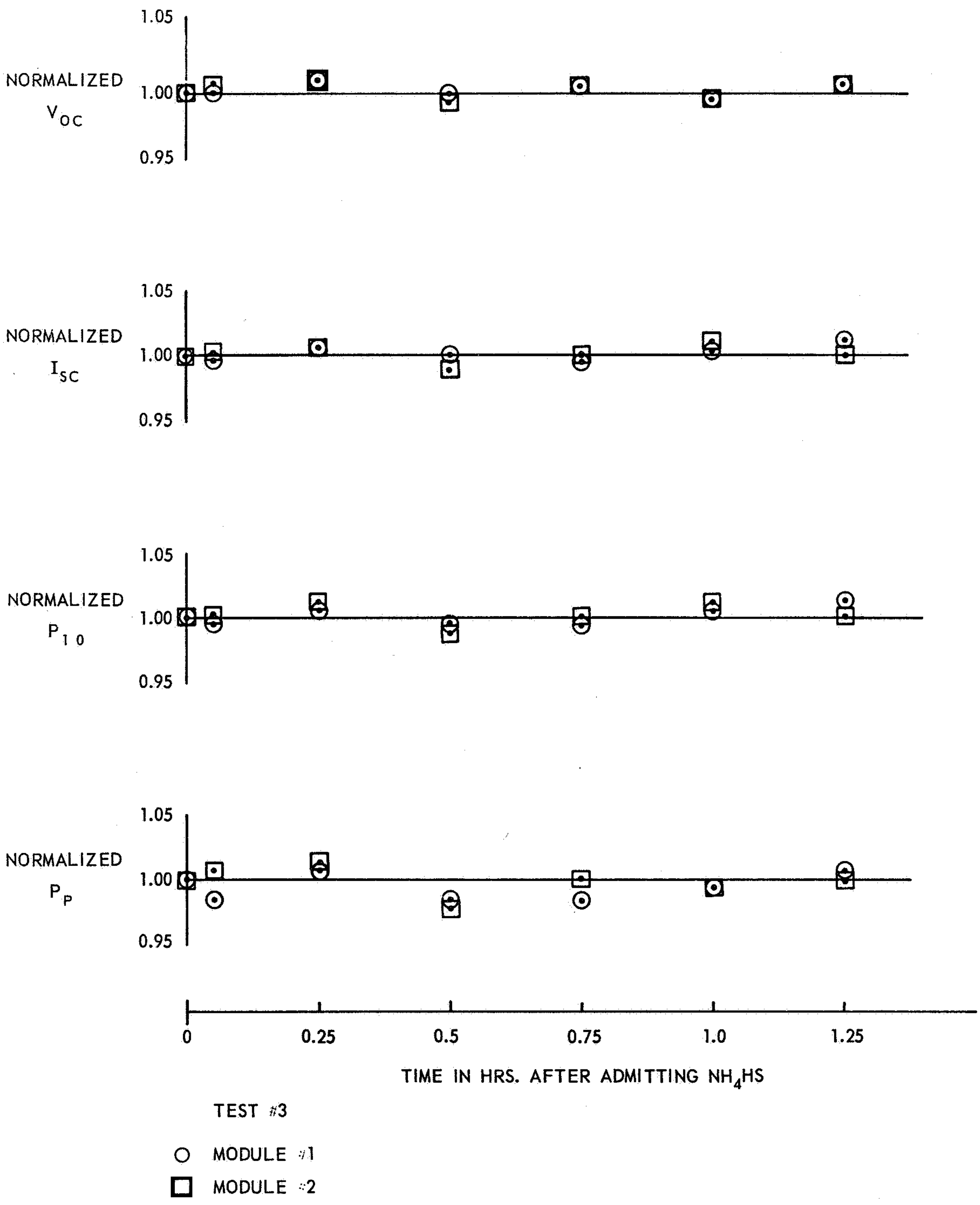

Figure 8. Normalized Electrical Parameters vs. Time for Modules Without Coverslides at −20°C

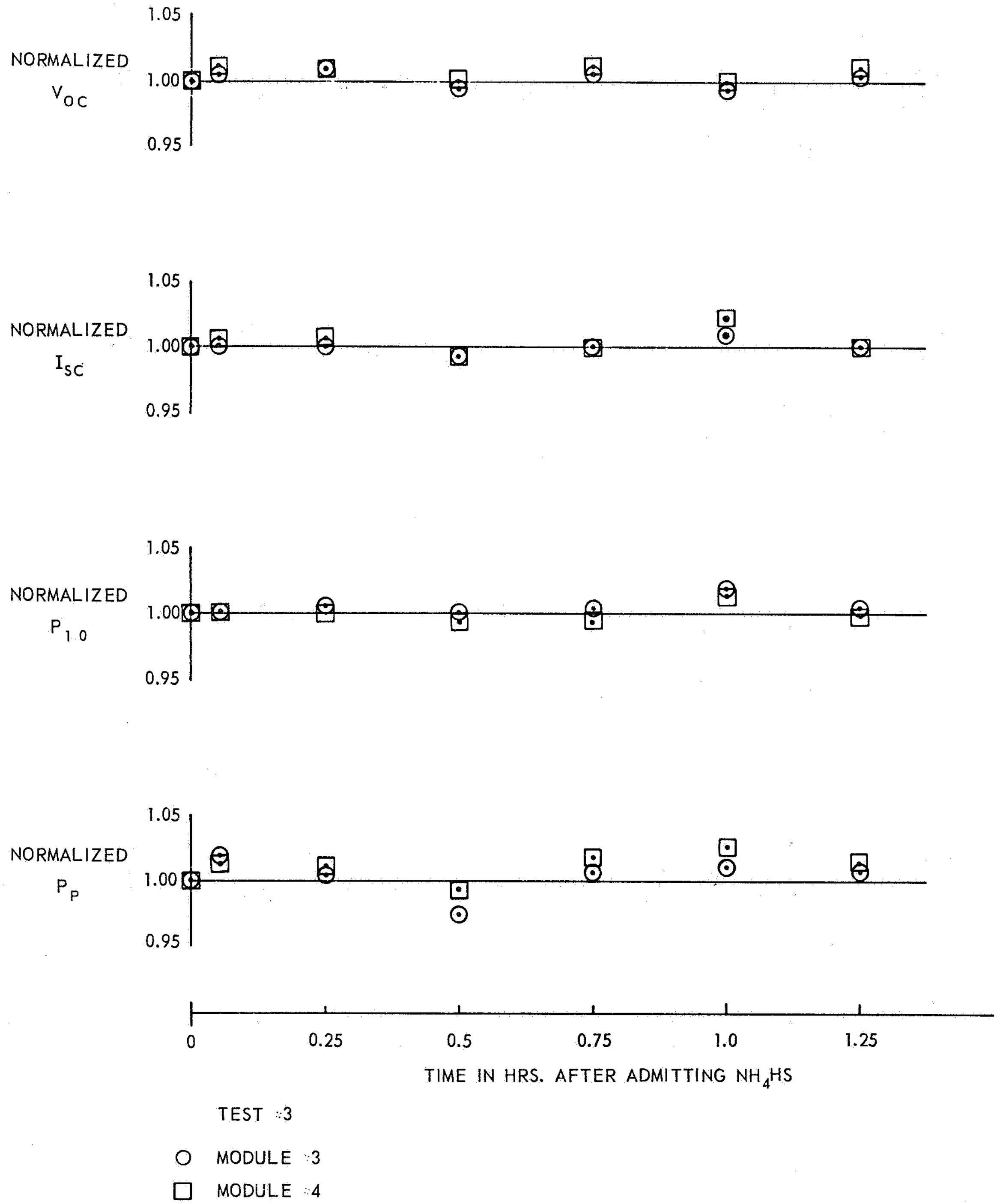

Figure 9. Normalized Electrical Parameters vs. Time for Modules With Coverslides at –20° C

these parameters, degradation would have been indicated but the increase, which was observed, can be most logically explained by a change in light intensity.

In test No. 2 the open circuit voltage increased to the limit of the error during the reading taken at 0.50 hrs. This was due to a temperature decrease in the modules from 0°C to about -6°C. All other data recorded during the investigation was well within anticipated experimental error.

It is apparent from examining the curves (Figures 4-9) that the electrical output, reflected in the short circuit current, the peak power and the power at 1.0 volt has not been affected by exposure to the hydrogen sulfide gas at any of the test temperatures and pressures. Further, if we compare readings taken at room temperature before exposure to the hydrogen sulfide gas with readings taken about 18 hours after the last test (Table 1) we observe a correlation of ±2% for the previously stated parameters. This is, of course, well within our anticipated experimental error.

Table 1

Comparison of Electrical Parameters Before and After Exposure to Ammonium Hydrogen Sulfide

	I_{sc} (ma)	V_{oc} (V)	P_1 (mw)	P_P (mw)	Temp (°C)
Module 1					
initial	100	1.62	89	99.3	24
final	101.5	1.62	91	101.8	25
% change	+1.5	0	+2.2	+0.8	—
Module 2					
initial	98	1.62	93	106.4	25
final	100	1.61	94	107.1	25
% change	+1	-0.6	+1.1	+0.7	—
Module 3					
initial	93	1.62	79	87.8	23
final	92.5	1.61	79	86.5	24
% change	-0.5	-0.6	0	-1.5	—
Module 4					
initial	94	1.62	92	106.4	23
final	94	1.61	92.5	107.7	25
% change	0	-0.6	+0.5	+1.2	—

Before the tests were begun each of the four active modules was thoroughly cleaned with alcohol and the physical status recorded. Upon removal from the vacuum chamber at the conclusion of the tests it was noted that the exposed silver was slightly brown in color. This became increasingly darker over a period of about one hour at room ambient conditions. Not all of the exposed silver turned brown yet some of the grids, covered by the glass cover slide, did turn. It is assumed, but not proven, that this was a result of an interaction of silver, hydrogen sulfide and moisture in the air.

Freon 14 Literature Survey Results

A literature survey of Freon gas disclosed that according to Reference 1, the "principal characteristics (of Freon gas) include nonflammability, a low level of toxicity, excellent thermal and chemical stability, ... The 'Freon' compounds in general are stable to a degree not ordinarily found in organic compounds... The more fluorine present the greater the stability." Freon 14 has more fluorine per molecule than any other of the Freon gases.

The E. I. Dupont Company in Reference 2 indicates that Freon 14 gas will not react with silver at the temperature where glass begins to soften.

Based upon this information it was felt that no laboratory investigation was warranted.

CONCLUSIONS

Since it is anticipated that the solar paddles will experience actual exposure to about 10^{-4} Torr pressure of hydrogen sulfide and the pressures experienced in this investigation were up to 10^{5} times as great as the anticipated values, it may be safely concluded that the solar paddles on the AIMP-E spacecraft will experience little or no short-term degradation as a result of the use of the proposed attitude control system using ammonium hydrogen sulfide.

The literature survey indicates that no damage to the solar array should be anticipated as a result of the use of the altitude control system which employs Freon 14 gas.

RECOMMENDATIONS

This investigation was conducted to determine if degradation of silicon solar cells in excess of 4 or 5 percent occurred over a period of a few hours and under tungsten light. Further, relatively low priority investigation should be conducted which would consider the following:

1. Refining the equipment and test procedures to increase confidence in the results.

2. Increasing the time parameter from a few hours to about one year.

3. Testing under sunlight conditions as opposed to tungsten light.

REFERENCES

1. Properties and Applications of the "Freon" Fluorocarbons (Dupont, Technical Bulletin No. B-2). Wilmington, Delaware, 1966.

2. Properties of "Freon-14" Fluorocarbon in the Gaseous State (Dupont, Technical Bulletin No. B-36). Wilmington, Delaware.

ACKNOWLEDGMENTS

The author wishes to thank the Mechanical Systems Branch of Goddard Space Flight Center for their cooperation in construction of the test chamber and Mr. R. H. Peterson for his assistance in conducting the experiment. Appreciation is extended to Mr. J. W. Thompson of the Solar Power Sources Section for his fine help in the fabrication of the test samples.

APPENDIX A

HYDROGEN SULFIDE

TOXICOLOGY

Hydrogen sulfide is both an irritant and an asphyxiant. Low concentrations of from 20 to 150 ppm cause irritation of the eyes; slightly higher concentrations may cause irritation of the upper respiratory tract, and if exposure is prolonged, pulmonary edema may result. The irritant action has been explained on the alkali present in moist surface tissues to form sodium sulfide, a caustic.

With higher concentrations the action of the gas on the nervous system becomes more prominent and a 30-minute exposure to 500 ppm results in headaches, dizziness, excitement, staggering gait, diarrhea and dysuria, followed sometimes by bronchitis or bronchopneumonia. The action on the nervous system is, with small amounts, one of depression; in larger amounts, it stimulates, and with very high amounts the respiratory center is paralyzed. Exposures of 800 to 1000 ppm may be fatal in 30 minutes, and high concentrations are instantly fatal. Fatal hydrogen sulfide poisoning may occur even more rapidly than that following exposure to a similar concentration of hydrogen cyanide. H_2S does not combine with the hemoglobin of the blood; its asphyxiant action is due to paralysis of the respiratory center.

With repeated exposures to low concentrations, conjunctivitis, photophobia, corneal bullae, tearing, pain and blurred vision are the commonest findings. High concentrations may cause rhinitis, bronchitis and occasionally pulmonary edema. Exposure to very high concentrations results in immediate death. Chronic poisoning results in headache, inflammation of the conjuncativae and eyelids, digestive disturbances, loss of weight and general debility.[1]

[1] N. Irving Sax, Dangerous Properties of Industrial Materials (New York: Reinhold Publishing Corporation, 1957), p. 770.