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Quarterly Report No. 4

STUDY OF FUEL CELLS USING STORABLE ROCKET PROPELLANTS

19 November 1965 to 18 February 1966

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by

R. F. Drake, L. F. Athearn, R. E. Chute
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Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS3-6476

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CONTRACT NAS3-6476

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SUMMARY

Of five possible systems investigated to produce H_2 from Aerozine-50, three have been tested in long-term, continuous runs. A multiple reactor steam reformer consisting of a 450°C prereactor, 750°C reformer, and a CO shift reactor was operated for 1000 hours at a H_2 efficiency above 95%. Enough H_2 was produced by this unit to continuously supply a fuel cell of more than 24 watts.

A low temperature (30°C) liquid phase reactor was tested for 700 hours until a catalyst plug blocked the piping leading from the reactor and caused a rupture. This unit decomposed 50% of the N_2H_4 in the input Aerozine-50 to H_2 initially, but gradually declined in performance. The usefulness of this approach with present catalysts is questionable.

The intermediate temperature (450°C) steam reformer actually was the prereactor in the multiple reactor unit. This reactor operated at 35% H_2 efficiency initially, but over 1000 hours declined in efficiency to 11 ± 3%. This drop in performance caused very little decline in the overall system efficiency of the multiple reactor unit, but does indicate that the usefulness of a single 450°C reactor is questionable.

The N_2O_4 decomposer (with 2% Pt catalyst) was operated for 1000 hours at 800°C with few problems. With N_2O_4 fed at 20g/hour, the conversion efficiency was 99% initially but dropped to 80-85% after 80 hours. Enough O_2 was produced by this unit to continuously supply a 24-watt fuel cell.

The operation of a 1/3 ft^2 N_2O_4 cathode was demonstrated after many mechanical problems were solved. This cathode produced 22 watts at a coulombic efficiency of 27% at 30 amperes total current. This is nearly an order of magnitude improvement over results reported previously. The improvement can be ascribed to a new reactant flow plate design.

Similar results have not been obtained with Aerozine-50 anodes. Several new electrode types have been tried, but none has performed satisfactorily.

Author

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I. INTRODUCTION

A. BACKGROUND

The objective of this research is to develop fuel cell systems operating on storable rocket propellants as primary or secondary reactants.

The present contract calls for the investigation and development of cells operating on gaseous N_2O_4 and Aerozine-50 as direct reactants, and for a reforming capability to use these reactants to produce O_2- and H_2-rich feedstreams for fuel cells. The construction and operation of working reformers and cells are the objectives of this work. Work on prior contracts in this investigation has been published (ref. 1 and 2).

B. PROGRAM ORGANIZATION

The project consists of three phases, to be performed roughly in series. The overall work plan shown in Figure 1 illustrates the major tasks to be performed. Detailed working plans for Phase I were illustrated in previous reports. Working plans for Phase II are shown in Figure 2.

C. SCOPE OF THIS REPORT

This report covers work done to complete Phase I and to begin Phase II. The following Phase I tasks are reported here; all others are considered completed:

(1) 1000-Hour Test on Aerozine-50 Steam Reformer.

(2) Long-term testing of low temperature Aerozine-50 decomposer.

(3) 1000-Hour Test of N_2O_4 catalytic reactor.

(4) Characterization of 1/3 ft^2 N_2O_4 cathodes - direct reactant use.

(5) Development of Aerozine-50 anodes - direct reactant use.

(6) Development of analytical procedures.

The following Phase II tasks are discussed:

(1) The demonstration of an N_2H_4 vapor electrode.

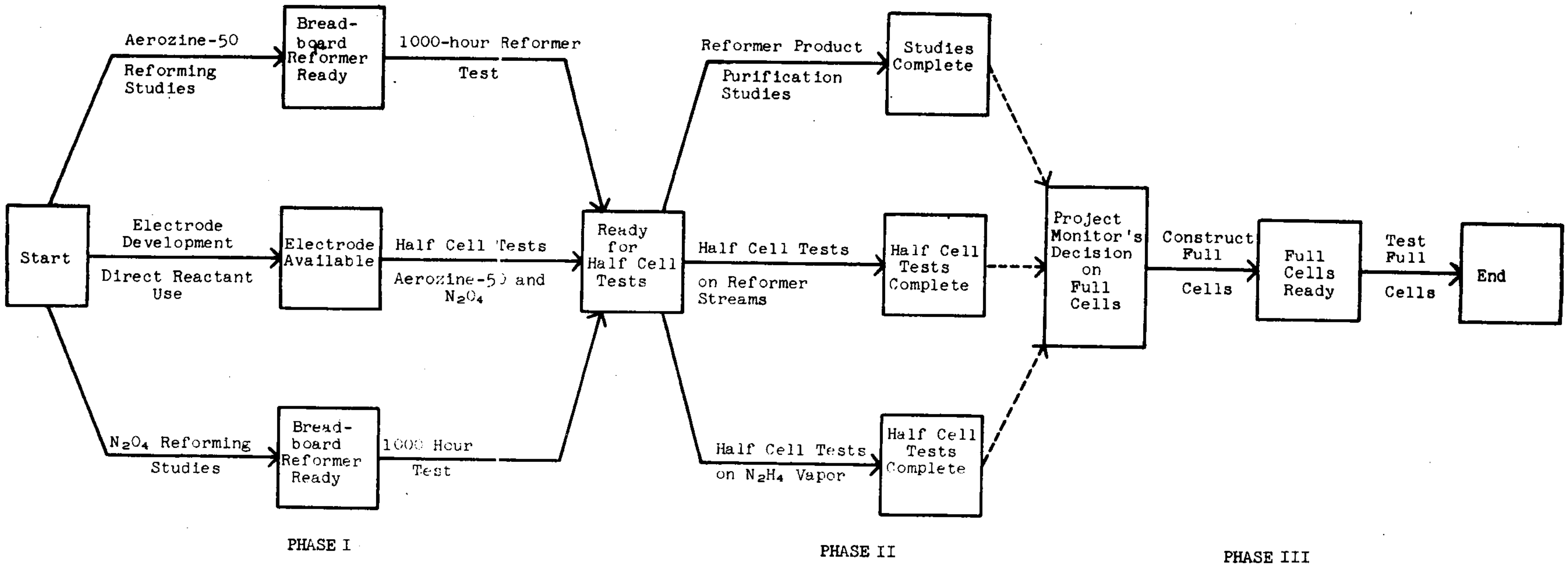

Figure 1. PROGRAM WORK PLAN AND EVENT CHART
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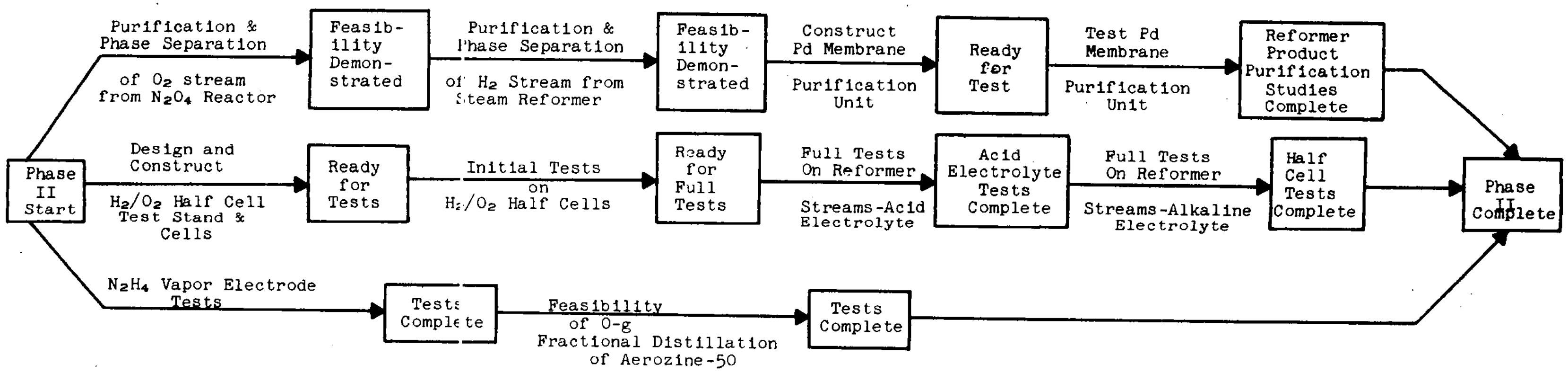

Figure 2. NAS3-6476 PHASE II WORK PLAN

(2) The feasibility of separating N_2H_4 from Aerozine-50.

(3) The construction of H_2/O_2 half cell testing facility.

II. PHASE I, TASK I. AEROZINE-50 REFORMING STUDIES

A. BACKGROUND

The objective of this task is to produce in a simple catalytic flow reactor a hydrogen-rich fuel cell feed stream from a 50 wt-% N_2H_4, 50 wt-% UDMH (Aerozine-50) feed stream at a maximum efficiency and at reasonably low temperatures.

Five systems have been investigated that allow tradeoffs between H_2 efficiency, temperature, simplicity, and the composition of the output stream. These are (1) low temperature, liquid phase catalytic decomposition; (2) intermediate temperature (450°C) steam reforming; (3) intermediate temperature steam reforming followed by an NH_3 decomposer; (4) high temperature (600-800°C) steam reforming; and (5) high temperature steam reforming with a CO shift reactor. As shown in previous reports, each system was developed to the point where a determination of its feasibility was possible. Based on these tests three systems were chosen for long-term testing: (1) the low temperature decomposer, (2) intermediate temperature steam reforming, and (3) high temperature steam reforming with CO shift. Work this quarter involved the long-term testing of these systems.

B. LOW TEMPERATURE, LIQUID PHASE DECOMPOSITION

Decomposition at atmospheric pressure and 30-50°C is potentially the simplest and most straight-forward method of producing H_2 from liquid Aerozine-50. Only the N_2H_4 component of the fuel can make significantly large contributions to H_2 production, and this limits the efficiency to a maximum of 32%.

Potential catalysts selected from an initial batch screening program were further tested in a tubular, continuous flow, liquid phase reactor. The reactor consists of a 2-ft length of 1/2-in. diameter stainless steel tubing, which contains the catalyst bed. The reactor tube is enclosed in a water jacket that is fed from a thermostatically controlled water bath. The feed stock is delivered to the reactor by a calibrated, positive displacement metering pump. A schematic diagram of the equipment is shown in Figure 3.

Initial tests of 4 to 6 hours' duration were performed on the best catalysts found in the batch screening program; the results of these tests were summarized in previous reports (ref. 3, 4, 5). Two catalysts, an MRC-developed Rh black on a special support, and a commercial reduced, stabilized Ni on Kieselguhr (Girdler T325), were promising enough for longer term tests.

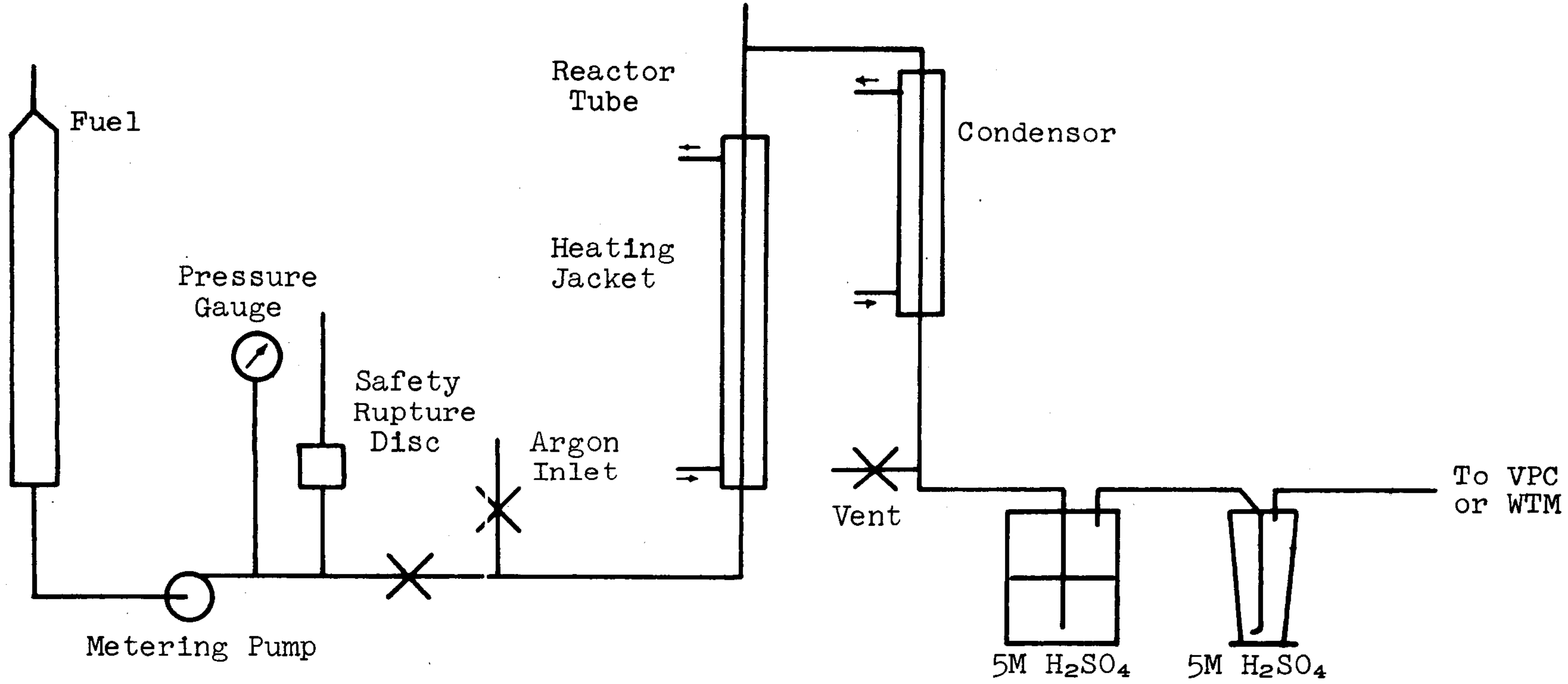

Figure 3. Aerozine-50 Liquid Phase Reactor Schematic

The Rh catalyst was found to decline in activity rather sharply over several days, when Aerozine-50 was the feed stock. A further test was made in which an N_2H_4-H_2O solution was used as the feed stock. This test, which was still in progress at the end of the last quarterly report period, was ended at 74 hours. At the end of the test the hydrogen efficiency was still 60% (based on the N_2H_4 content) indicating no deterioration of catalyst activity had occurred. This seems to confirm the suspicion that the UDMH portion of Aerozine-50 or reaction products of UDMH are the cause of deterioration of catalyst activity. This poisoning effect is lower at lower temperatures, but the rate of decomposition to H_2 is also lower, necessitating larger catalyst volumes or weights.

Long-term investigations were then run with Girdler T-325 catalyst (reduced, stabilized nickel in Kieselguhr) that had previously given 58% H_2 efficiency based on the N_2H_4 portion of the Aerozine-50 during a 20-hour test period at 30°C. At temperatures higher than 35°C this catalyst had declined in activity.

A test of 125 hours duration (see Table 1) with an Aerozine-50/H_2O solution (62.5% Aerozine-50 by weight) was made. The highest efficiency was 66.0% based on N_2H_4. After 86 hours the efficiency was still 64%. However, after this period, slow deterioration started, resulting in 50% efficiency after 124 hours.

The deterioration was due to lower rates of N_2H_4 decomposition, rather than NH_3 formation, as has previously been noted in this work. This was shown by the constant H_2/N_2 ratio in the product gas, and also by qualitative information on the amount of $(N_2H_4)_2H_2SO_4$ precipitate formed.

Based on these results, the Girdler T-325 catalyst was chosen for the 1000-hour test on this system. Aerozine-50 (without H_2O) was fed to the reactor at a rate 50% higher than in the previous test. It was found necessary to purge the reactor with H_2O at the start of the test to avoid poisoning the catalyst by the highly exothermic reaction caused by the sudden ingress of the fuel. Over a period of 1 day the H_2O was displaced by the Aerozine-50 and the reactor reached a steady state.

This test ran continously for 700 hours until the reactor tube ruptured because of an unrelieved over-pressure. Table 2 gives a complete history of the 700-hour test. The maximum H_2 efficiency (based on N_2H_4) of 56.5% was reached at 30.6°C, after 49 hours. From then on a slow deterioration occurred until the efficiency reached 32.3% at 316 hours. At that time the low efficiency was primarily caused by incomplete N_2H_4 decomposition

Table 1

LOW TEMPERATURE, LIQUID PHASE REACTOR LONG-TERM TESTS WITH GIRDLER T-325 CATALYST

Bed Volume 2.2 in^3

Running Time, hr	Temperature, °C		Composition, wt-%		Aerozine-50 Input Rate, g/hr	Output Gas Rate at 25°C, l/hr	VPC Analysis, mole-%		H_2 Efficiency,		Notes
	Water Jacket	Reactor Center	A-50	H_2O			H_2	N_2	Total Basis	N_2H_4 Basis	
2.0	30.5	27.5	62.5	37.5	6.75	6.6					
4.0	30.5	27.5	62.5	37.5	7.12	6.0	59.1	40.9	20.7	65.0	
6.0	30.5	27.5	62.5	37.5	6.99	5.8					
26.0	30.5	27.5	62.5	37.5	6.75	5.7	59.6	40.4	20.9	65.4	Ran overnight.
56.0	30.5	27.5	62.5	37.5	6.63	5.6					Ran overnight.
62.0	30.5	27.5	62.5	37.5	6.50	5.4	61.4	38.6	21.1	66.3	Shut down over 5-day period and restarted.
86.0	30.5	27.5	62.5	37.5	6.75	5.4	61.2	38.8	20.3	63.6	
100.0	30.5	27.5	62.5	37.5	6.99	4.7	62.0	38.0	17.3	54.2	
124.0	30.5	27.5	62.5	37.5	6.99	4.3	62.2	37.8	15.9	49.7	Deterioration due to less N_2H_4 decomposed, not NH_3 formation.

Table 2.

LIQUID PHASE REACTOR 1000 HOUR TEST

Bed Volume = 2.21 in^3 Catalyst = Reduced Stabilized Ni on Keisselguhr, 3/16 in. tablets

Running Time, hrs	Temp. °C	Aerozine -50 input rate, g/hr	Output Gas Rate at 25°C, 1/hr	V.P.C. Analysis, Mole %			H_2 Efficiency		Notes
				H_2	N_2	Other	Total Basis	N_2H_4 Basis	
6	26.8	9.74	4.70	61.6	38.4	-	12.3	38.6	Started with 20 ml H_2O in reactor, at normal pumping rate of 11 ml/hr.
25	26.6	9.97	3.66	61.6	38.4	-	9.9	31.0	
28	30.0	9.97	6.05	61.6	38.4	-	15.5	48.6	
31	30.3	9.97	6.46	61.6	38.4	-	16.6	51.9	Takes one day to reach equilibrium
49	30.6	9.69	6.83	61.6	38.4	-	18.0	56.5	Some undecomposed N_2H_4 in output
55	30.6	9.69	6.75	59.9	40.1	-	17.3	54.3	
124	30.3	9.69	5.47	62.1	37.9	-	14.5	45.6	On over weekend
148	30.3	9.88	5.45	61.2	38.8	-	14.0	43.9	eff. drop due to less N_2H_4 decomposed, not NH_3 formation
172	30.7	10.09	5.23	61.2	38.8	-	13.1	41.2	
196	30.6	9.74	4.99	61.2	38.8	-	13.0	40.8	
220	30.3	9.63	4.71	61.2	38.8	-	12.4	38.9	
292	31.0	9.92	4.55	62.1	37.9	-	11.8	37.1	On over weekend
316	31.0	9.62	3.81	62.7	37.3	-	10.3	32.3	
364	31.5	9.60	3.28	57.4	42.6	-	8.1	25.5	Eff. drop mostly due to less N_2H_4 decomposition
460	32.0	9.79	2.70	61.2	38.8	-	7.0	22.0	On over weekend
484	33.5	9.13	3.05	60.9	39.1	-	8.5	26.5	Raising temp to attempt to increase eff.
508	35.0	8.93	3.39	60.8	39.2	-	9.6	30.0	
628	37.0	8.95	3.18	60.8	39.2	-	9.0	28.1	On over weekend
652	40.8	9.31	3.90	57.7	40.8	1.5	10.0	31.4	CO_2 noticed on VPC, not sure whether true or contaminant.
672	40.5	9.41	3.57	57.7	41.9	0.4	9.1	28.5	
676	42.2	9.41	4.21	58.2	41.1	0.7	10.8	33.9	
696	42.4	8.98	3.64	58.2	41.1	0.7	9.8	30.7	
700	45.6	9.81	5.04	55.3	44.7	-	11.8	37.0	Most of N_2H_4 decomposed, more NH_3 being formed. Overnight reactor burst.

rather than NH_3 formation. The temperature was subsequently raised in small steps in an attempt to increase efficiencies. It was found that the reaction rate would increase for a time after each increase in temperature, but would then decline again. Finally at 700 hours, a rate equal to 37.0% was found at 45.6°C. However, nearly all the N_2H_4 was decomposed, indicating that a shift toward NH_3 formation had also occurred at the high temperature. This was confirmed by the lower H_2/N_2 VPC ratio occurring at 45.6°C.

Shortly after 700 hours, during overnight operation, the reactor burst. This was evidently caused by deterioration of the catalyst, which plugged the reactor, presumably at the reduction joint from 1/2 inch to 1/4 inch tubing at the reactor end. The pressure build-up caused the 200 psig rupture disk to blow. This should have saved the reactor tube from rupture. However, it seems likely that when the rupture disk burst, the catalyst plugged the bottom of the reactor tube at the reduction joint from 1/2 inch to 1/8 inch size, causing the reactor to plug at both ends. The decomposition of Aerozine-50 left in the catalyst bed thus occurred in a sealed tube, which eventually ruptured.

It is evident from the data generated during this test that the Ni-base catalyst used will not be satisfactory for this application both because of its physical disintegration and, more importantly, because of its loss in activity in long-term testing. Accordingly, a short screening program was initiated in an attempt to find a more active catalyst. The following catalysts were tested for short periods (1 to 2 days) in the reactor:

Harshaw Zn0701 (24% ZnO on activated alumina)

Girdler G-47 (Fe_2O_3; support unknown)

" G-49A (Reduced, stabilized Ni on Kieselguhr)

" G-49B (Reduced, stabilized Ni on Kieselguhr).

None of these catalysts showed any advantage over the T-325 catalyst.

Further catalyst screening was done in the small batch reactor described in previous reports (ref. 3). In this reactor smaller amounts of catalyst could be used and the screening tests could be run much more rapidly. Liquid Aerozine-50 is added dropwise into a thermostated flask containing the catalyst. The volume of gas produced is measured and a sample is taken for VPC analysis. Ratios of H_2/N_2 substantially lower than 2:1 in the sample indicate NH_3 formation. The results of these tests are presented in Table 3.

Table 3

CATALYST SCREENING RESULTS FOR DECOMPOSITION OF AEROZINE-50

Temperature: 30°C.

Catalyst and Support	Mole % H_2	Mole % N_2	Activity	Comments
Pt on carbon substrate	58.3	40.2	low activity	some NH_3
Rh on carbon substrate	69.4	30.6	active	little NH_3
Rh black powder	69.5	30.5	active	" "
Harshaw Ni-W sulfide (pellets)	-	-	inactive	
5 component precious metal alloy catalyst on carbon substrate	61.3	38.7	very active	slight amount NH_3
NiB catalyst	-	-	inactive	
Ir on carbon substrate	1.1	98.9	very active	mostly to NH_3
Ru on carbon substrate	9.7	89.9	active	mostly to NH_3
Cu chelate of ethylene Bisdithiocarbamate	-	-	no activity	
Co chelate of ethylene Bisdithiocarbamate	-	-	no activity	
Ni chelate of p,p'-diphenylene Bisdithiocarbamate	-	-	no activity	
Cu chelate of hexamethylene Bisdithiocarbamate	-	-	no activity	

The chelate catalysts were tried because of published reports of highly specific catalytic effects with N_2H_4 (ref. 6). They were carefully prepared by published techniques (ref. 7, 8), washed with pyridine to remove soluble portions, and vacuum dried before testing. The single-component precious metal catalysts were made from standard commercial blacks incorporated in our MRD-carbon/catalyst electrodes which were subsequently cut up into small squares for testing. The NiB and the 5-component alloy were made in our laboratory. The Harshaw Ni catalyst was a commercial product.

The only new catalyst showing any promise in these tests was the 5-component precious metal alloy*. Even this catalyst did not demonstrate any advantage over the previously tested Rh catalyst in this short-term testing.

C. HIGH TEMPERATURE SYSTEMS

Long-term testing on both the intermediate temperature and the high temperature steam reformers was done in a single experimental set-up; the intermediate temperature reformer essentially served as a pre-reactor for the high temperature reformer, which, in turn, fed the CO shift reactor. A schematic diagram of the equipment is shown in Figure 4. Preliminary testing was reported in our previous quarterly report (ref. 6). Before the start of the 1000-hour test, several modifications were made. These modifications included:

(1) A safety device to shut down the system if hoods were to fail.

(2) Temperature control to shut down the system if reactors should go out of control.

(3) A safety device to shut down system in case of fire.

(4) A modification of system to permit stream composition determination after the first reactor.

(5) A second rupture disk bypassing the solenoid valve controlling the back pressure in reactor 1.

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* Developed under a company-sponsored program.

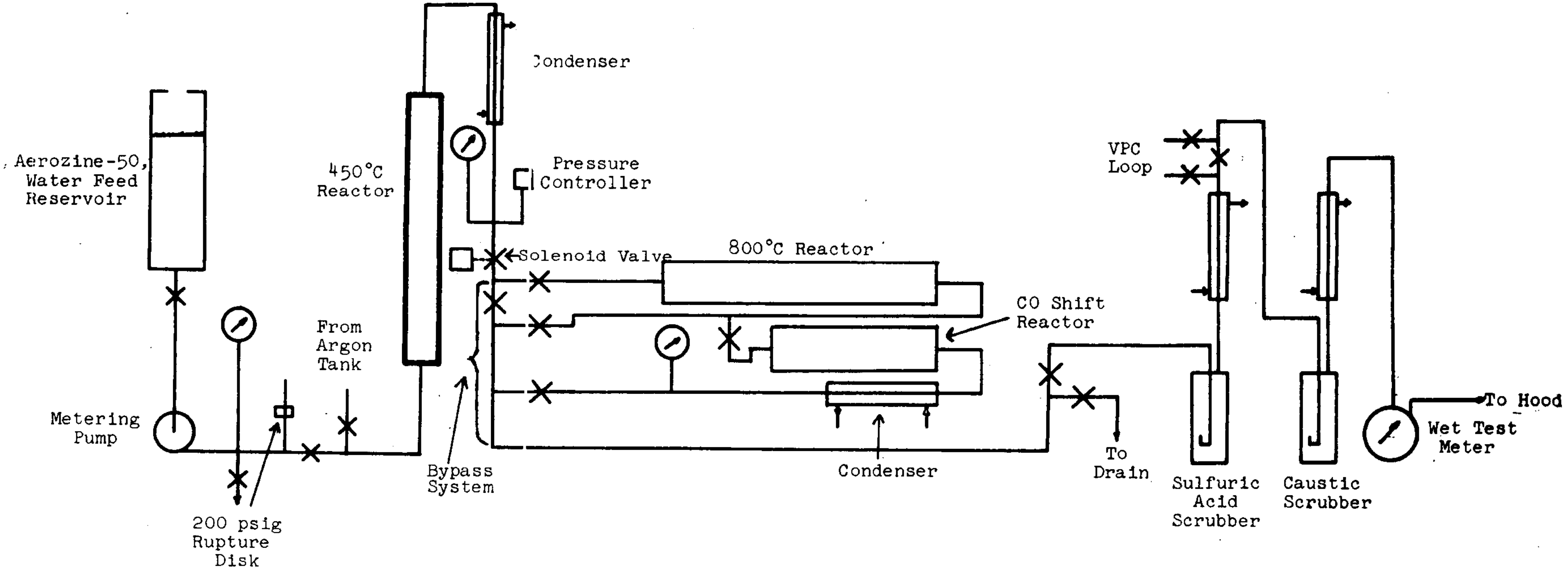

Figure 4. Aerozine-50 Multiple Reactor Schematic

(6) Better temperature control and measurement on the CO shift reactor.

(7) A third rupture disk installed in the inlet side of reactor 2 to vent in case of blockage in piping leading to reactor (installed midway in 1000-hour test).

The 1000-hour test was started 16 December 1965. The complete history of this test including operating parameters is reported in Table 4., and the details on each analytical determination are included in Appendix I. The modest decrease in H_2 efficiency (from 98.7% to 95.6%) over the life of the test was caused by slight decreases in NH_3 decomposition and in steam reforming (CH_4 content higher). After 1000 hours the NH_3 in the output stream corresponded to only 3% of available nitrogen, and the CH_4 content to 2.4% of available carbon. The theoretical equilibrium composition listed at the bottom of Table 4, was calculated by a computer program (Appendix II). The final output composition is very close to the theoretical values and indicates that near equilibrium conditions were obtained even after 1000 hours of testing.

The H_2 efficiency of the first reactor (at 450°C) at the start of the test was 35%. The efficiency declined to 28% after 50 hours and subsequently to 11 ± 3% at 1000 hours. However, the ability of the high temperature reactor to accept a large variation in composition of the feed stream is shown by the fact that the overall system efficiency declined very little. This is an indication of the reliability that could be obtained in such a multiple reactor system.

Three equipment problems were encountered during the test period that required short-term shut down's of the system. The down time was substracted from the total running time. At about 500 hours a blockage occurred in the 1/4 in. tubing entering the 800°C reactor. The blockage was due to carbon deposition in an area where the gas stream passed through a large thermal gradient. This particular piece of tubing had been in service throughout the screening tests. Thus the amount of carbon deposition in 1000-hour test cannot be determined. In an integral reactor, no such blockage could occur if there were no piping constrictions leading to the high temperature reactor.

At 580 hours another blockage occurred, this time due to a build up of ZnO in the condenser that cools the products from the first reactor. We do not believe the ZnO catalyst in the reactor was physically disintegrating since no evidence of this was found when the catalyst was examined after completion of the test. Since no blockage occurred in the line leading to the

Table 4

1000 HOUR TEST OF HIGH TEMPERATURE STEAM REFORMER

Input Composition = 64.3% H_2O, 35.7% A-50 by weight; H_2O/C Mole Ratio = 6.0

Total Input Rate = 19.5 to 21.5 ml/hr; 7.25 to 7.65 gm/hr A-50

Reactor No.	Function	Press, Psig	Temp, °C	Catalyst
1	Prereactor	50	445-450	G-72, 100% ZnO, 1/8 in. extr.
2	Equil. Steam Reforming and NH_3 Decomp.	5	770-800	G-56B, Ni base, 1/8 in. tablets
3	CO Shift	5	255-275	G-66B, Promoted Fe_2O_3, 1/8 in. tablets

Reactor Tubes are 1 in. O.D. and 3/4 in. I.D.

Time, hrs	Hydrogen eff.	Amp - hr H_2 per Hr.	Total Mass Balance	Output Composition, Mole %							Composition to Fuel Cell after Stripping H_2O, NH_3 & CO_2 (Mole %)			
				H_2O	NH_3	CH_4	H_2	CO	CO_2	N_2	H_2	N_2	CH_4	CO
72	98.7	36.35	99.6	31.4	<.1	0	48.2	0.1	8.6	11.7	80.2	19.4	0	0.2
247	96.5	37.04	99.9	33.1	0.2	0	46.7	0.1	8.1	11.8	79.7	20.1	0	0.2
335	96.8	34.26	99.4	33.9	0.3	0	46.4	0.2	7.4	11.8	79.6	20.1	0	0.3
557	95.0	37.08	98.1	33.4	0.9	0	46.3	0.1	8.2	11.2	80.4	19.4	0	0.2
662	96.4	35.63	100.2	32.9	0.8	0.1	46.5	0.1	8.2	11.4	80.0	19.6	0.2	0.2
859	96.2	37.70	100.2	32.8	0.7	0.2	46.5	0.2	8.2	11.4	79.8	19.6	0.3	0.3
1000	95.6	33.55	101.7	33.5	0.7	0.2	46.1	0.2	7.8	11.5	79.5	19.9	0.3	0.3
Theoretical Output Composition				32.7	<0.1	<0.1	47.5	0.2	7.9	11.7				

Note: for 24 watt fuel cell at 100% H_2 eff Amp/hr/hr needed = 26.63
at 80% H_2 eff Amp/hr/hr needed = 33.29

condenser, it is possible that the material was carried to the condenser as Zn vapor, which condensed and then was oxidized to ZnO by H_2O. It has been suggested by others (ref. 9) that H_2 and CO can reduce ZnO to Zn, which has a much higher vapor pressure than ZnO. Even though the presence of H_2O in the reactor should prevent this reaction, nonhomogenous areas in the reactor bed may exist, and eventually enough Zn could be produced and carried away to cause the blockage. In an integral reactor no blockage would occur if the stream were initially cooled in a relatively large diameter tube. The amount of ZnO lost from the reactor by this process is actually infinitesimal and would have no effect on the reactor performance.

The pumping of the Aerozine-50-water solution into the reactor system has been difficult with the small input rates used. At first the pump could not be kept running for longer than 15 to 20 hours. Apparently, slight N_2H_4 decomposition takes place on the walls of the inlet tubing and in the pump itself. At the low pumping rate, this causes a gas bind in the pump, and no liquid is transferred. The fuel system has been modified to eliminate most of the decomposition products before they get to the pump, and 48 to 64 hours of operation are now possible without pump stoppage. However, the input rate gradually decreases with time from 21.5ml/hr to 19.5ml/hr over this period. This causes difficulty in analyzing H_2 efficiency.

D. TASK STATUS

This task is considered complete and no further work is anticipated. We have demonstrated a combined steam reforming-CO shift reactor system that produces with high efficiency a fuel cell gas feed stream composed of 70mole-%H_2, 18mole-%N_2, 12mole-%CO_2 (after separation of the excess H_2O). The CO content of the stream is 0.3mole-% or less. This stream could be fed directly to a fuel cell with a CO_2 rejecting electrolyte (either acid, carbonate or acid ion exchange membrane). If the CO_2 content of the stream were scrubbed out, the stream could be used with any fuel cell electrolyte. A CO- tolerant anode catalyst such as those developed under another MRC contract (ref. 10) would be necessary. If a Pd membrane purification unit were used, the stream could be used with any H_2 utilizing fuel cell since completely pure H_2 stream would result.

The results with the liquid phase reactor are not as promising because of the drop in efficiency experienced with the best catalysts tested. A feasible system for this application may depend upon a periodic regeneration of the catalyst (e.g., a periodic flush with H_2O), and the development of a physically stronger catalyst. The intermediate temperature reactor (the pre-reactor in the multiple system) also showed a marked decrease in performance that was due to a gradual build-up of carbon deposits on the catalyst. This situation could undoubtedly be improved by higher H_2O contents in the feed stream and larger amounts of catalyst.

III. PHASE I, TASK II. DECOMPOSITION OF N_2O_4

A. BACKGROUND

The objective of this task is to decompose N_2O_4 by means of homogeneous and catalytic reactions in a simple flow reactor to form an oxygen-rich feed stream for a fuel cell. The initial work (described in previous reports) involved screening 41 catalysts for activity, however, none were found with any activity below 750°C. Following the screening program, several catalysts were selected for further studies in which the activity was determined over a more extended period. At the completion of these tests only the 2% platinum-on-alumina catalyst retained sufficient activity to be considered promising. The work accomplished this quarter involved the long-term testing and characterization of this catalyst.

B. PRELIMINARY TESTING

The reactor system was modified for long-term testing. The final system used is shown schematically in Figure 5. The operation of this reactor is similar to the screening test reactor operation described in previous reports except that the residence time in this reactor has been quadrupled by connecting the reactor tubes in series.

Preliminary testing was concentrated on determining the optimum operating conditions to be used with the Engelhard 2% Pt-on-alumina catalyst. Another objective was to check the operation of the system during extended continuous service. The results of these tests are shown in Figure 6.

Several conclusions can be drawn from this testing. First it is apparent from the data that the reactor temperature cannot be reduced much below 800°C without a drop in conversion efficiency. Also, some decline in conversion efficiency with time was noted, indicating some reduction in catalytic activity.

Two other conditions became evident as this test proceeded, which required some changes in the test methods. A more accurate means for determining the per cent N_2O_4 decomposed was required. This was found in an acid titration method using H_2O_2 to convert all the N_2O_4 to HNO_3 (Appendix III). Both input and output rates were measured in this manner.

The second of these conditions is shown in Figure 6, which indicates greater than 100% decomposition efficiencies were obtained when the feed rates were reduced. It is apparent that the system had not reached steady-state conditions when the

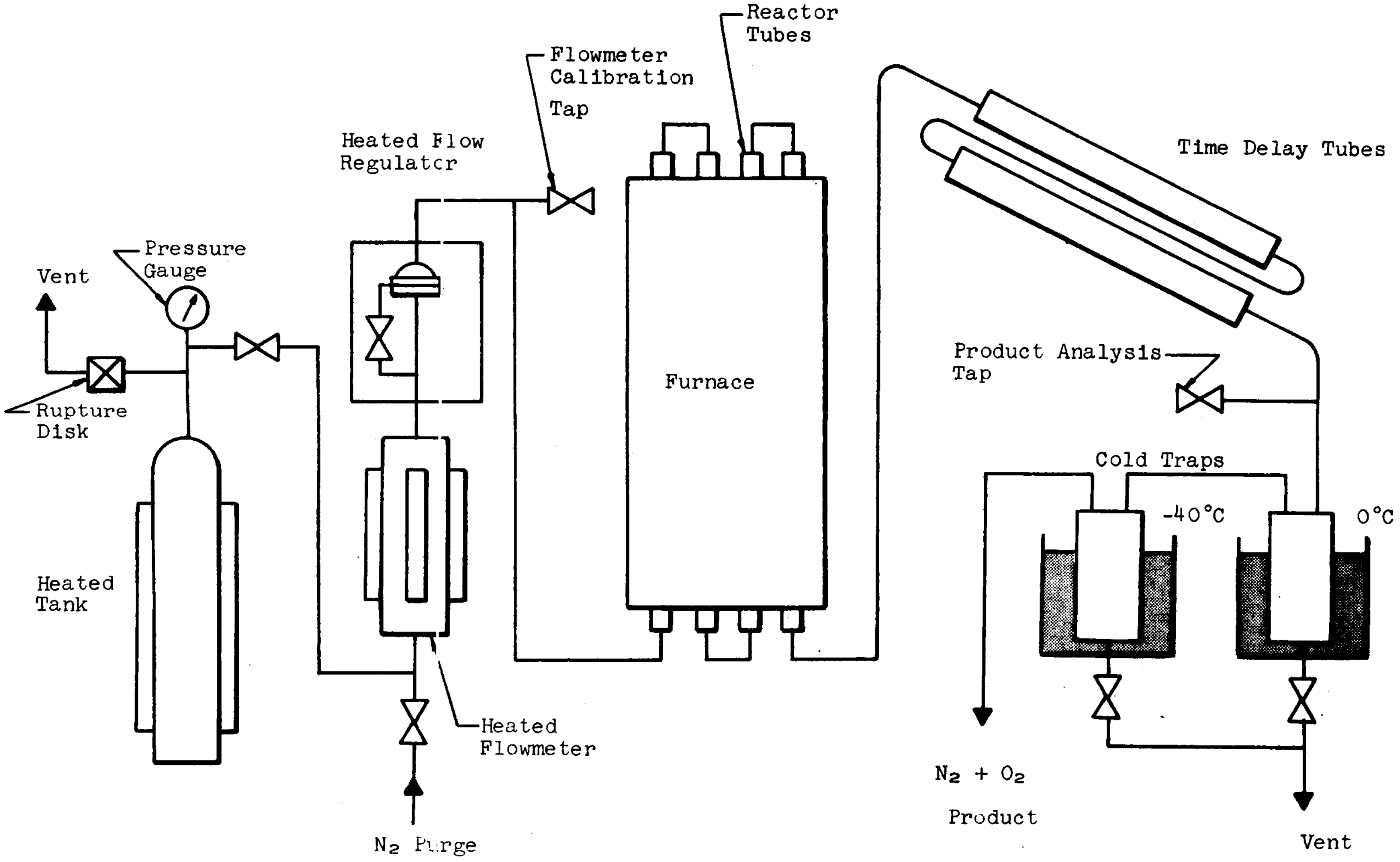

Figure 5. N_2O_4 REACTOR SYSTEM SCHEMATIC

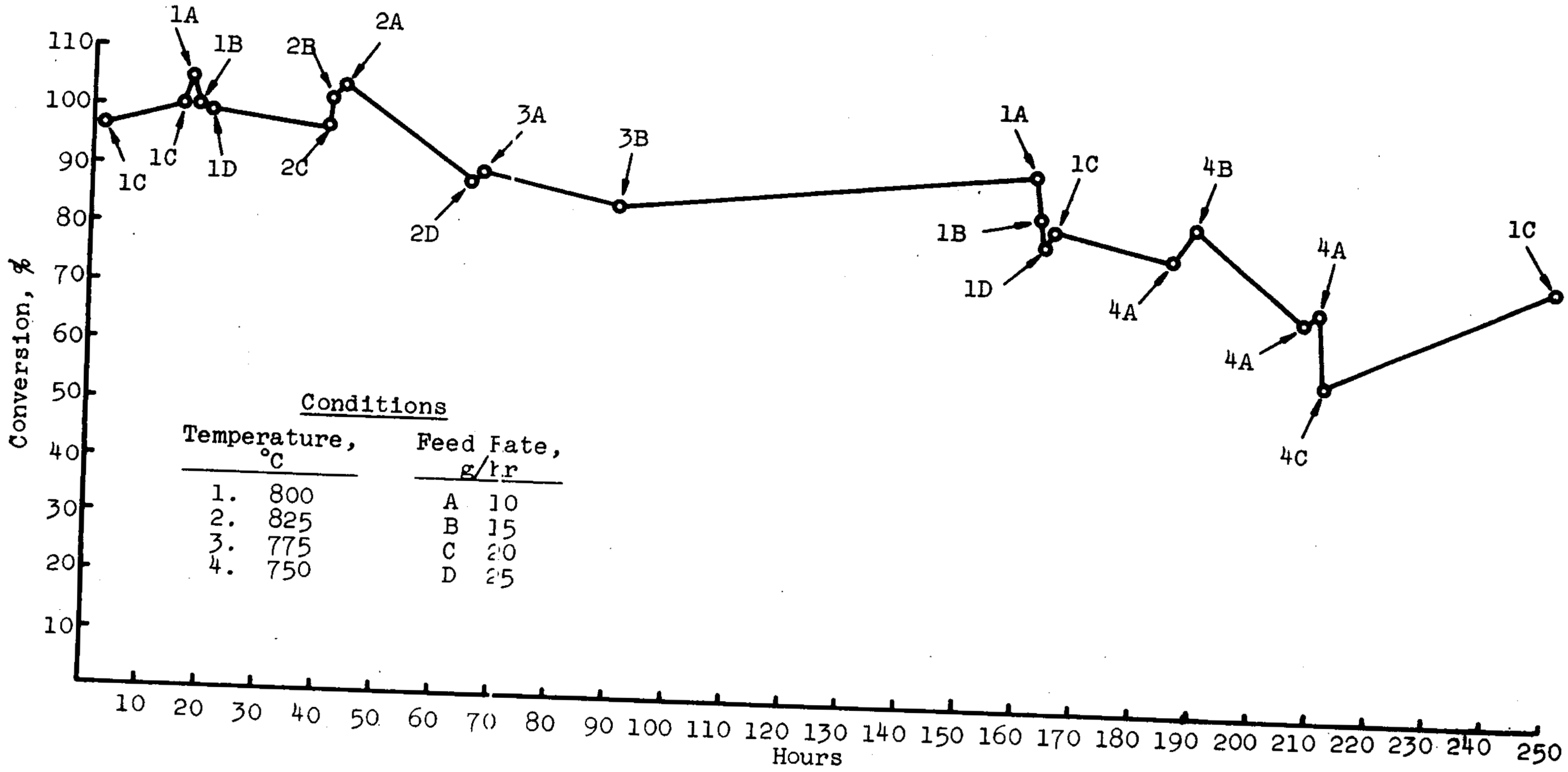

Figure 6. Conversion Efficiency versus Operating Time For 2% Pt Catalyst

measurements were made. An analysis of the operating conditions in the reactor system indicates that a long time period may be required for steady-state conditions to be attained after a change in temperature or reactant flow rate. The factors that play a major role in the slow equilibration of the system after a change in conditions are the shift in the location of the reaction sites, changes in the gas phase and adsorbed phase composition, and changes in the catalyst activity associated with these composition changes. It is estimated that complete equilibration of the system may require as long as 16 to 24 hours after a change in operating conditions.

C. 1000-HOUR TEST

The 1000-hour test was started on 15 December 1965 using four reactor tubes in series containing a total of 324 grams of 2% platinum catalyst. Each reactor tube was fitted with a thermocouple in the center of the catalyst bed. The standard test conditions selected were 800°C with a feed rate of 20 g of N_2O_4 per hour. Conversion efficiencies were determined by sampling both the input and output streams and analyzing for N_2O_4 by the peroxide acid titration method. Very few mechanical problems were encountered. A thermocouple burned out in one of the tubes after 750 hours and had to be replaced. Less than one hour of down time resulted.

The conversion efficiency obtained under the standard conditions during the 1000-hour period is shown in Table 5.

TABLE 5

N_2O_4 REACTOR CONVERSION EFFICIENCY
AT 800°C, 20 GRAMS N_2O_4 FEED/HR

Time hr	N_2O_4% Converted	
60	99	
80	79	
250	85	
470	79	
675	76	
750	72	(Thermocouple replaced)
900	80	
975	80	
1000	79	

After 80 hours of operation catalyst activity declined as indicated by the decline in the N_2O_4 conversion efficiency (from 99 to 79%). Shifts in the individual reactor internal temperature were also noted at this time. At the beginning of the test all of the reactors were within 10°C of 800°C. After 80 hours the temperature of first reactor tube had dropped to 765°C, the second tube remained at 800°C, the third had risen to 845°C, and the fourth tube was at 810°C. It is possible that the temperature variations indicate a shift in the predominant reaction in the first reactor to simple reactant heating plus decomposition:

$$NO_2 = NO + 1/2O_2 \text{ (endothermic)}$$

The exothermic decomposition of NO in the following sections explains the temperature increase in these reactors.

After the conversion efficiency had stabilized, the effect of residence time was determined by varying the feed rates over the range of 6 to 29 g N_2O_4/hour. At least 16 hours was allowed for equilibration before conversion data were taken. The results of these tests are shown in Figure 7. It is apparent that much longer residence times or catalyst volumes will be required for conversion efficiencies above 85%. The two extreme points on this curve were rechecked after the 1000-hour test was completed and were within experimental error of the earlier results. The curve is much flatter than expected, and it is unlikely that 97% or greater conversion efficiency can be obtained with a reasonable amount of catalyst. The data fit a second-order plot reasonably well, indicating that the overall reaction is second order with respect to N_2O_4.

D. TASK STATUS

This task is considered complete and no further work is planned. We have demonstrated an N_2O_4 decomposer that will convert 80-85% of input N_2O_4 to a gas stream consisting of a 2:1 mole ratio of O_2 to N_2. The output stream is contaminated with unconverted N_2O_4 and probably could be used directly only in a contained electrolyte or free acid electrolyte cell. Some HNO_3-HNO_2 will be formed in this electrolyte, but the dissolved N_2O_4 would be in equilibrium with NO in the exhaust stream and would be consumed electrochemically so that a steady state concentration would result. We have demonstrated previously that a Pt- containing H_2 anode can operate in such a contaminated electrolyte. However, an acid ion exchange membrane cell probably could not be used with this stream because of oxidative attack on the membrane.

For use in an alkaline or ion exchange membrane cell, the stream must be purified.

We had expected to demonstrate greater than 97% conversion efficiency by providing increased residence time in the reactor. This would have demonstrated the feasibility of scrubbing the stream with a column containing molecular sieves

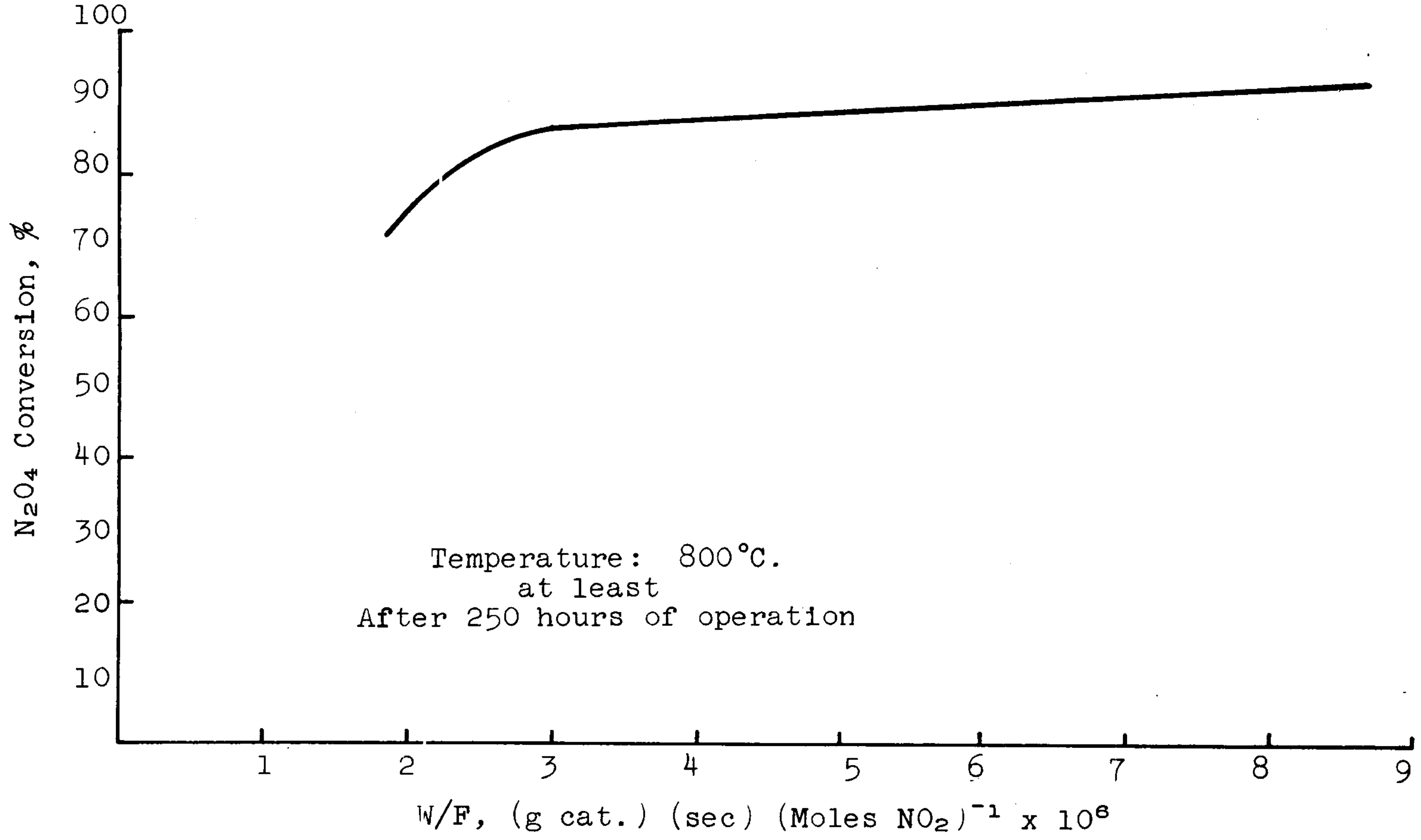

Figure 7. Conversion vs Time Factor for N_2O_4 Reactor

or KOH pellets. At 80-85% conversion, however, this method is not feasible for any reasonable operating time because the weight of the scrubber would be too high. Figure 7 indicates that the weight of catalyst required to reach 97% conversion would also be prohibitive. For example, at an 80% conversion only 16.4 lb of catalyst would be required to supply a 1 KW fuel cell module with O_2. For 97% efficiency, this figure is over 100 lb of catalyst.

Two alternate methods are available to purify the stream. A double molecular sieve column could be used in which one side is used to scrub the feed stream while the other side is regenerated by venting to the space vacuum (possibly with heating). The other method involves the use of the excess water separated from the Aerozine-50 steam reformer product stream. The water will quantitatively absorb the N_2O_4 from the decomposer stream, and a simple phase separation would produce a stream capable of being used in any fuel cell.

IV. PHASE I, TASK III. DIRECT REACTANT USE

A. BACKGROUND

The objectives of this task are to develop electrode structures and techniques that will allow the direct utilization of gaseous N_2O_4 and Aerozine-50 (50 wt-% N_2H_4, 50 wt-% UDMH) as reactants in a fuel cell. A further requirement is that these reactants be used efficiently in a single pass through the electrode chamber of the fuel cell.

The N_2O_4 cathode was developed and demonstrated under a previous contract (ref. 2) and, although the polarization characteristics were excellent, the coulombic efficiencies were quite low. The objectives during this contract are to improve the coulombic efficiencies and to demonstrate the electrode in 1/3 ft^2 cell size. As reported in the previous Quarterly Report, the reduction of a substantial portion of the N_2O_4 oxidant to N_2 rather than NO has been shown with our MRD-carbon electrode.

Liquid Aerozine-50 has been investigated as a fuel cell reactant in the same temperature range used for the N_2O_4 cathode work.

B. N_2O_4 CATHODE

1. General

During this quarter the 1/3 ft^2 N_2O_4 cathodes have been more fully characterized. Figures 8 and 9 show the half cell construction and the reactant flow plate design used. The cells were assembled and tested with a controlled, measured N_2O_4 flow rate. A H_2 "dummy" anode was used and current was controlled with a power supply.

2. Problems Encountered

Many problems were encountered in operating a cell of this size. Some of these problems are discussed in the following paragraphs.

a. Water Balance

A cell was constructed utilizing a gelled electrolyte made from a 5M phosphoric acid and colloidal silica gel. An ion exchange membrane (Ionics 61AZL183) was inserted between the gelled electrolyte and the "dummy" H_2 anode to isolate the cathode section and insure the validity of the analytical data.

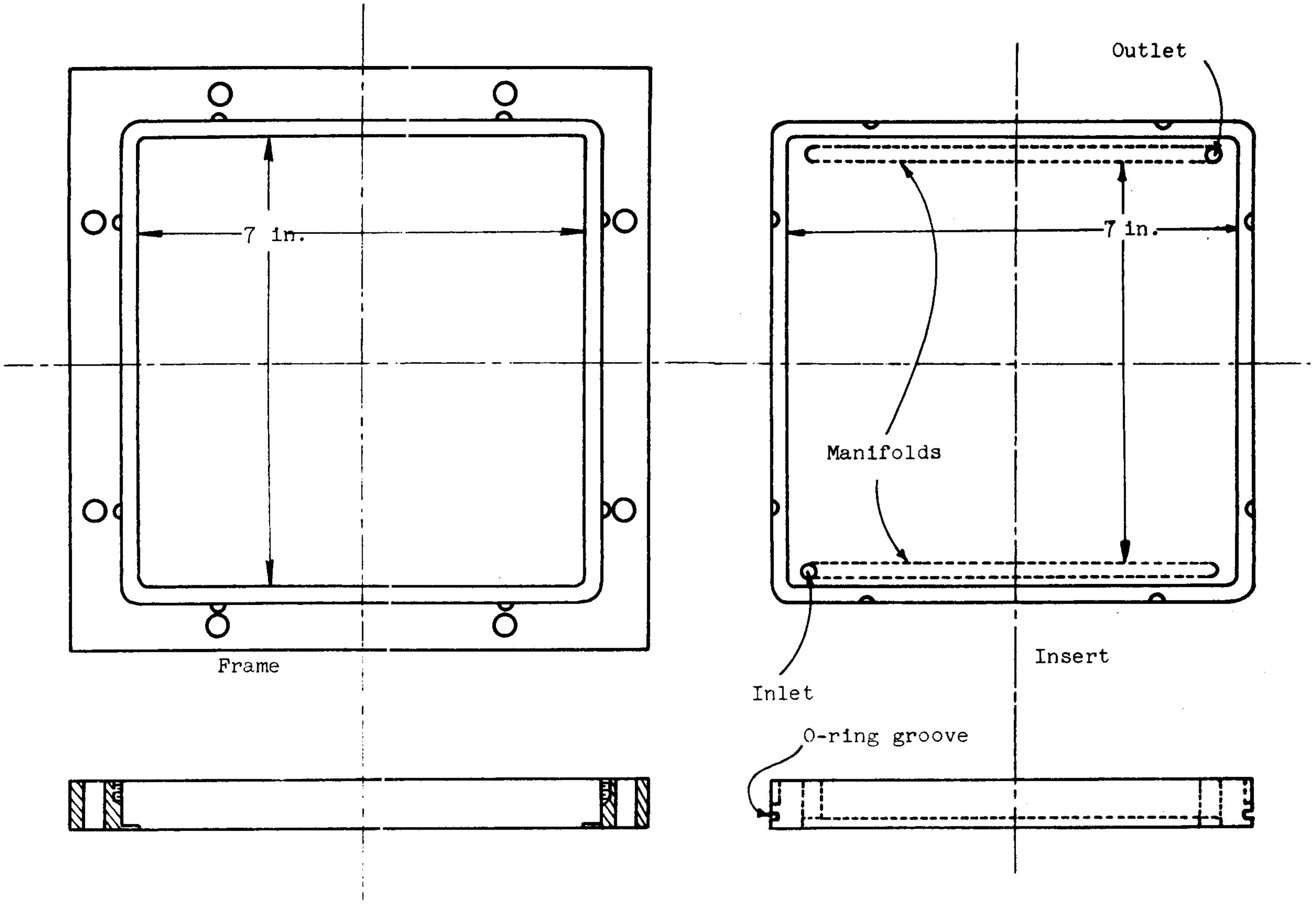

Figure 3. 1/3 ft^3 Test Cell Construction

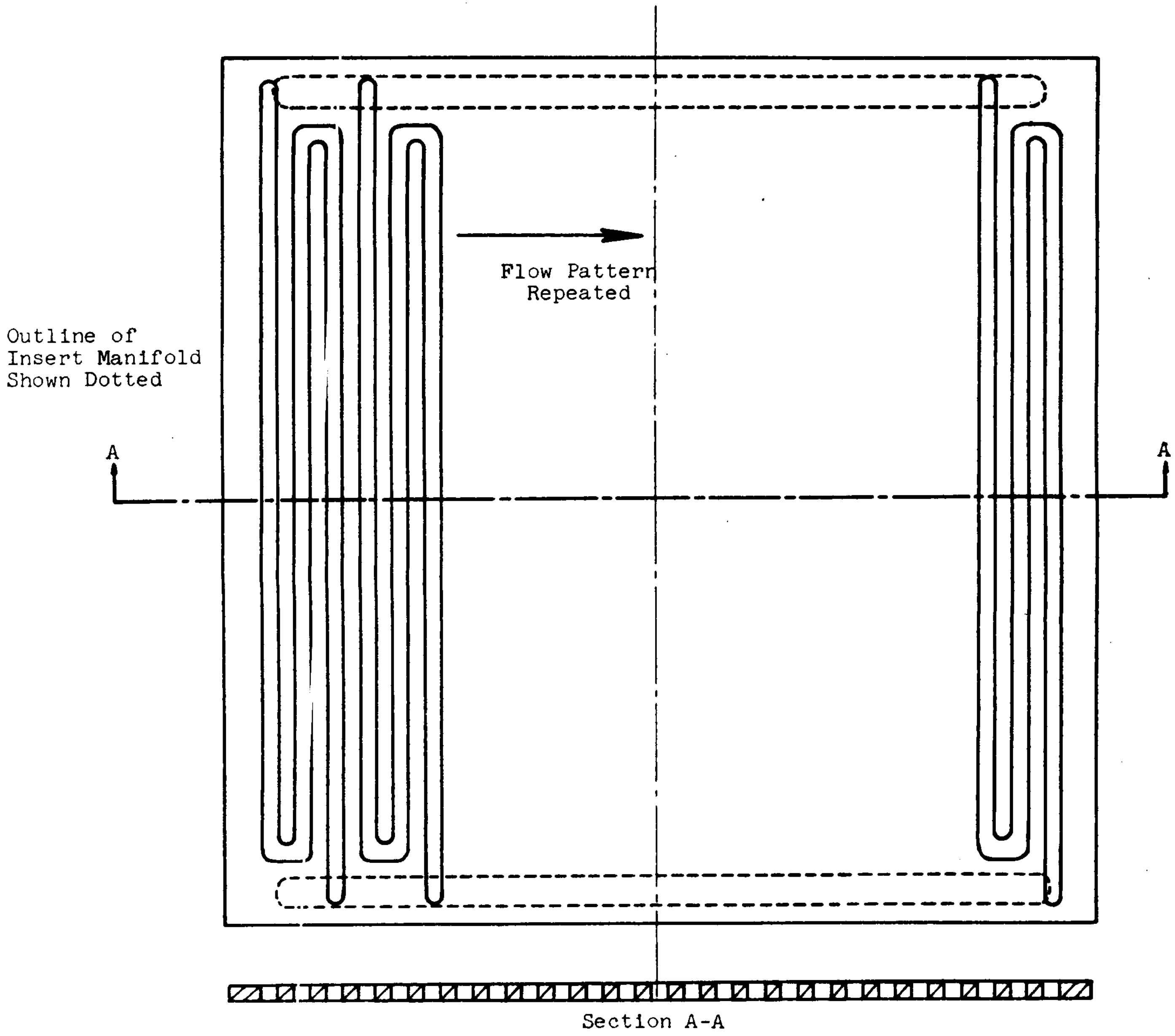

Figure 9. Reactant Flow Plate

The reference electrode used with these cells consisted of a small plastic tube inserted in the gel near the electrode surface filled with 5M phosphoric acid leading to a pot of the same acid in which a calomel electrode was inserted. This method worked very well at low current densities (30 amp/ft^2 and below). When the current density was increased to 60 and 100 amp/ft^2, gas pressure built up in the cell and bubbled out through the reference electrode tube.

The tube was then packed with the same phosporic acid gel as was used for the cell electrolyte. With this type of reference electrode reproducible cathode voltages were obtained at 11 current densities up to 100 amp/ft^2. Typical values at 60°C are shown below:

	30 amp/ft^2	60 amp/ft^2	100 amp/ft^2
initial	0.95	0.95	-0.35
1 Hour	0.94	0.28	-0.65

The reasons for the severe polarization at the higher current densities and longer operating times were not obvious until the cell was taken apart. The gelled catholyte had dried out and had shrunk away from large areas of the cathode, indicating a high water removal rate. It was also found that the cathode was not pressed firmly against the flow control plate, thus reducing the N_2O_4 velocity and distribution on the back of the cathode.

The results of these tests argued for a free electrolyte cell in which a large volume of electrolyte is circulated through the cell to maintain a water balance. It was also apparent that more compression on the electrode was necessary to insure an adequate seal to the reactant flow plate. The cell was subsequently redesigned to use a pumped electrolyte with a series of screens against the electrode to supply the necessary compression. The final configuration used is shown in Figure 10.

b. Electrolyte Pumping

In operating the redesigned cells it was quickly found that the stainless steel pumps that had rotating gland type seals leaked excessively when the phosphoric acid electrolyte was heated to the cell operating temperature. Replacement of the standard seals with Teflon seals did not stop the leakage. New seal-less magnetically driven, centrifugal pumps were found to be necessary for extended operation.

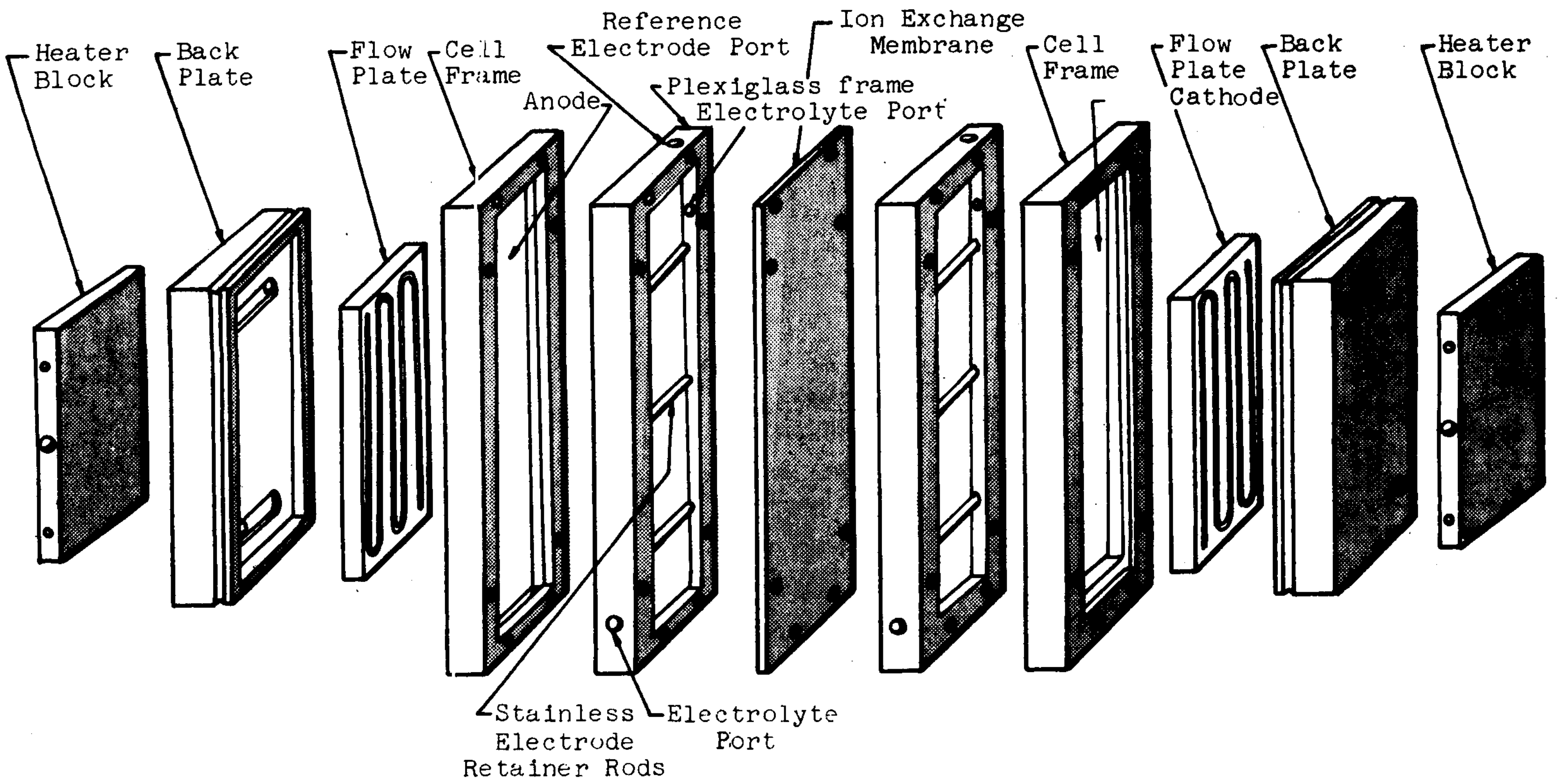

Figure 10. N_2O_4 1/3 Ft^2 Test Cell.

c. Reference Electrodes

When the pumped electrolyte cells were operated, some of the product gases (N_2 and NO) were discharged into the electrolyte. These gas bubbles interfered with reference electrode measurements by acting as an intermittant open circuit. A new arrangement was tried in which the reference electrode was connected to the cell by a Teflon tube containing a glass wick saturated with electrolyte. The end of the glass wick was spread over a thin polyproplyene paper separator that was placed on the cathode surface. This design worked satisfactorily.

d. Analysis of Reaction Products

The gaseous products of the cell reaction exit the cell in both the electrolyte and cathode exhaust stream. Both of these streams must be analyzed to obtain a complete material balance. The electrolyte stream contains nitrogen and nitric oxide. Quantitative tests were not made on the gases but the qualitative tests performed indicated mostly nitrogen and very little nitric oxide was present.

The stream exiting from the back side of the operating cathode contains N_2O_4, NO, N_2 and H_2O and has proven extremely difficult to analyze. However, the overall coulombic efficiency of the electrode can be determined because the both N_2O_4 input rate and the total electrical current withdrawn from the electrode are known accurately. Since there is direct evidence that N_2 is the predominant reaction product, the coulombic efficiencies were calculated on the basis of complete reduction to N_2.

A pumped electrolyte cell constructed as described above was assembled with a 0.050 in thick cathode flow plate and mounted in the test stand. Over a period of a week this cell was operated intermittently at various temperatures and N_2O_4 flow rates. Table 6 summarizes the results of these tests.

The results given in Table 6 are representive of cathode performance that can be expected after one hour at each of the test conditions and therefore are assumed to be steady state conditions. It may be noted that the performance at 70°C is much better than at 60°C at the same current densities. This difference was noted on many occasions and is thought to be due to changes in the diffusion rate of water and reaction products through the cathode. There is also a considerable reduction in performance when the N_2O_4 feed rate is reduced

TABLE 6.

N_2O_4 CATHODE HALF CELL ELECTRICAL PERFORMANCE

	Current Amp	Voltage Volts	N_2O_4 Used, %	Watts	N_2O_4 Input*
60°C	10	1.04	9.2	10	3.7x
	20	0.49	18.2	9.8	
	30	-0.20			
70°C	10	1.12	9.2	11	3.7x
	20	0.90	18.2	18	
	30	0.72	27.3	22	
70°C	10	1.03	13.7	10	2.5x
	20	0.35	27.3	7.0	
	30	-0.13	41.0		

---

* Times Stoichiometric amount for complete reduction to N_2 at 30 amps.

from 3.7 to 2.5 times the stoichiometric amount for 30-ampere operation.

In the course of making these measurements the cell was operated over a period of five days during which it was heated and cooled several times. The data points shown above were rechecked on several occasions and found to be reproducible.

The cell will be reassembled using a 0.025 in. thick reactant flow plate and a characterization test run. Higher N_2O_4 utilization and better performance at 60°C is expected with the 0.025 in. flow plate.

C. AEROZINE-50 ANODE

The results of testing both liquid Aerozine-50 and liquid anhydrous N_2H_4 were discussed in previous reports. When tested with MRD-carbon/Pt electrodes, liquid anhydrous N_2H_4 performed as well as H_2 gas in short-term testing. However, Aerozine-50 demonstrated poor polarization characteristics, which indicated that the major reactant at the electrode surface was UDMH. Since the Aerozine-50 vapor is composed primarily of UDMH, in the temperature range considered it appears that the carbon layer on this electrode was acting as a vapor diffusion membrane. Other membranes that would allow more liquid diffusion were tested, but none were found to be practical.

During this quarter several new types of electrodes were tested. The test cell used was a 9 in.^{2} free electrolyte cell with a reference electrode arrangement similar to that described for the N_2O_4 cathode half cell. The Aerozine-50 fuel was metered to the back of the electrode through a manifolding arrangement that insured an excess of fuel.

The results of these tests are given in Table 7. None of these electrodes performed satisfactorily on Aerozine-50 and none is considered worth following up.

Another approach was taken to this problem. Theoretically, Aerozine-50 can be fractionally distilled to separate its components. If even a partial distillation could be accomplished to obtain a relatively enriched N_2H_4 feed stock, the carbon/Pt electrode (or an equivalent) might be feasible. The major problem will be separation of phases (liquid N_2H_4 and vapor UDMH) under zero-gravity conditions. We have investigated a number of membranes for this application.

Liquid Aerozine-50 was circulated beneath porous membranes with reduced pressure on the other side.

Table 7

RESULTS OF ELECTRODE TESTS WITH AEROZINE-50

Electrode	Description	Results of Tests on Aerozine-50	Electrical Performance
MRD-carbon/Pt	Proprietary electrode consisting of 40mg Pt/cm^2 on carbon-teflon substrate, supported on stainless steel screen.	Will operate as a vapor diffusion electrode for 20-30 min, then completely wetted with Aerozine-50 and operates as liquid diffusion anode Pt layer disrupted and blistered.	Poor-heavy polarization.
Chemcel-hydrophobic	9mg Pt/cm^2 on a Ta mesh screen, Teflon hydrophobic layer applied by unspecified "new method".	Too porous - allows direct mixing of fuel and electrolyte with precipitation of hydrazine phosphates.	Could not be tested.
Chemcel + added porous Teflon	Above electrode mated with a sheet of porous Teflon - 0.050 in thick, 6.6µ average pore size.	Operated immediately as liquid diffusion anode - demonstrated for circa one hour - some physical degradation evident after test.	+0.32v vs SHE at 50 ma/cm^2, 30°C.
American Cyanamide LAF 1	Pt-RH catalyst deposited on a porous Teflon backing.	Delaminated and physically degraded (blistered) due to effects of decomposition of fuel.	Could not be tested.

Membranes tested included:

- -- MRD Carbon Electrode
- -- Molecular Sieve-Teflon Electrode
- -- Porous Stainless Steel Plaque, 2-5μ pore size
- -- Porous Teflon (0.3μ, 6.6μ, 11.7μ)

All of these membranes, except the molecular sieve electrode, were wetted by the Aerozine-50, which passed through as a liquid phase. Thus the separation could not be achieved. The molecular sieve electrode crumbled after about 1 hour of treatment with Aerozine-50 and thus was not suitable. Very little vapor transport occurred before the membrane disintegrated. It is possible that with a non-watering membrane the separation can be achieved. Increased temperature could also be used instead of reduced pressure for a driving force, which might cause less physical attrition of the membranes.

D. TASK STATUS

We have successfully obtained a greatly improved N_2O_4 cathode coulombic efficiency primarily as a result of the design of an efficient reactant flow plate. The efficiencies reported here are nearly an order of magnititude better than those reported on our previous contract (ref. 2). The cathode has been demonstrated in a 1/3 ft^2 size at practical current densities. This part of the task is considered complete.

The same degree of success has not been realized with the Aerozine-50 anode despite testing of a variety of electrode structures for this service. Those electrodes with satisfactory electrical characterisitcs invariably also caused excessive self-decomposition of the fuel and/or precipitation of hydrazine phosphates due to mixing of fuel and electrolyte.

An electrode operating from pure anhydrous N_2H_4 has been successfully demonstrated and could be developed for fuel cell service with an N_2O_4 cathode. A more promising system, however, is a H_2/N_2O_4 cell with the H_2 supplied by the Aerozine-50 steam reformer. We have previously shown that the H_2 anode is compatible with this cathode.

V. FUTURE PLANS

We intend to complete Phase II work (Figure 2) within the next quarter. At present, construction of a test stand for H_2/O_2 half cell testing on reformer streams is proceeding. The cells, pumps, controls and associated equipment will be installed and initial tests will be run on tank H_2 and O_2 to check the system. The reformers will be refurbished and the cells will then be run on the reformer streams. Both the input and output streams will be analyzed during operation of the cells. Both H_3PO_4 and KOH electrolytes will be tested.

The purification studies on reformer streams will involve:

(1) Running a Pd membrane purification unit on the steam reformer output. The test stand for this experiment is presently under construction.

(2) Demonstrating the feasibility of scrubbing the N_2O_4 reformer stream to remove undecomposed N_2O_4.

(3) Demonstrating the feasibility of separating the excess H_2O from the high temperature steam reformer stream.

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APPENDIX I

AEROZINE-50 STEAM REFORMING

DATA SHEETS

AEROZINE-50 STEAM REFORMING DATA SHEET, 1000 HR TEST

System Test No. 1

Catalysts 1st G-72 2nd G-56B 3rd G-66B

Notebook Reference No.

Temperature, °C 445, 790, 275

Reactor No. after last reactor

Pressure, psig 50, 5, 5

Cumulative Time of Catalyst Operation 72 hours

Gas Volume Rate 23.77 l/hr (25°C)

Moles Gas Produced/hr 0.9662

% N_2H_4 Used 100

% UDMH Used 100

	UDMH	H_2O	N_2H_4	Total
Feed Composition, mole-%	6.72	80.67	12.60	100.0
Feed Composition, g/hr	3.429	12.352	3.429	19.21
Feed Composition, mole/hr	0.0572	0.686	0.1071	0.8503

Total Output Composition, mole-%

UDMH 0 NH_3 <0.1 N_2 11.7 CO_2 8.6

H_2O 31.4 Dimethylamine 0 CH_4 0 Ethane 0

N_2H_4 0 H_2 48.2 CO 0.1 Other 0

Average Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

H_2 70.2 N_2 17.1 CH_4 0 CO 0.2 CO_2 12.6 Ethane 0

% H_2O Used: 35.8 % Reforming to CO_2: 106.4 % to CO: 1.7

Moles NH_3 Formed/Hr: 0.0008 by Keldahl

Moles H_2 per 100 g Aerozine-50 input: 9.89

Moles H_2 per 100 g Total Input: 3.53

Hydrogen Efficiency = 98.7%

AEROZINE-50 STEAM REFORMING DATA SHEET, 1000 HR TEST

System Test No. 2

Notebook Reference No. ______

Reactor No. after last reactor

Cumulative Time of Catalyst Operation 247 hours

Catalysts 1st G-72 2nd G-56B 3rd G-66B

Temperature, °C 445, 790, 275

Pressure, psig 50, 5, 5

Gas Volume Rate 24.29 l/hr (25°C)

Moles Gas Produced/hr 0.9874

% N_2H_4 Used 100

% UDMH Used 100

	UDMH	H_2O	N_2H_4	Total
Feed Composition, mole-%	6.72	80.67	12.60	100.0
Feed Composition, g/hr	3.658	13.174	3.658	20.49
Feed Composition, mole/hr	0.0610	0.7319	0.1143	0.9072

Total Output Composition, mole-%

UDMH	0	NH_3	0.2	N_2	11.8	CO_2	8.1
H_2O	33.1	Dimethylamine	0	CH_4	0	Ethane	0
N_2H_4	0	H_2	46.7	CO	0.1	Other	

Average Output Gas Composition:

(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

H_2 70.0 N_2 17.7 CH_4 0 CO 0.2 CO_2 12.1 Ethane 0

% H_2O Used: 32.9 % Reforming to CO_2: 98.0 % to CO: 1.6

Moles NH_3 Formed/Hr: 0.0036 by Keldahl

Moles H_2 per 100 g Aerozine-50 input: 9.45

Moles H_2 per 100 g Total Input: 3.37

Hydrogen Efficiency = 96.5%

AEROZINE-50 STEAM REFORMING DATA SHEET, 1000 HR TEST

System Test No. 3

Catalysts 1st G-72 2nd G-56B 3rd G-66B

Notebook Reference No. ______

Temperature, °C 445, 790, 275

Reactor No. after last reactor

Pressure, psig 50, 5, 5

Cumulative Time of Catalyst Operation 335 hours

Gas Volume Rate 22.244 l/hr (25°C)

Moles Gas Produced/hr 0.9043

% N_2H_4 Used 100

% UDMH Used 100

	UDMH	H_2O	N_2H_4	Total
Feed Composition, mole-%	6.72	80.67	12.60	100.0
Feed Composition, g/hr	3.373	12.148	3.373	18.894
Feed Composition, mole/hr	0.0562	0.6749	0.1054	0.8365

Total Output Composition, mole-%

UDMH 0 NH_3 0.3 N_2 11.8 CO_2 7.4

H_2O 33.9 Dimethylamine 0 CH_4 0 Ethane 0

N_2H_4 0 H_2 46.4 CO 0.2 Other 0

Average Output Gas Composition:

(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

H_2 70.7 N_2 17.8 CH_4 0 CO 0.3 CO_2 11.3 Ethane 0

% H_2O Used: 30.7 % Reforming to CO_2: 90.9 % to CO: 2.4

Moles NH_3 Formed/Hr: 0.0041 by Keldahl

Moles H_2 per 100 g Aerozine-50 input: 9.48

Moles H_2 per 100 g Total Input: 3.38

Hydrogen Efficiency = 96.8%

AEROZINE-50 STEAM REFORMING DATA SHEET, 1000 HR TEST

System Test No. 4

Notebook Reference No.

Reactor No. after last reactor

Cumulative Time of Catalyst Operation 557 hours

Catalysts 1st G-72, 2nd G-56B, 3rd G-66B

Temperature, °C 445, 790, 275

Pressure, psig 50, 5, 5

Gas Volume Rate 24.195 l/hr (25°C)

Moles Gas Produced/hr 0.9835

% N_2H_4 Used 100

% UDMH Used 100

	UDMH	H_2O	N_2H_4	Total
Feed Composition, mole-%	6.72	80.67	12.60	100.0
Feed Composition, g/hr	3.722	13.406	3.722	20.850
Feed Composition, mole/hr	0.0620	0.7448	0.1163	0.9231

Total Output Composition, mole-%

UDMH	0	NH_3	0.9	N_2	11.2	CO_2	8.2
H_2O	33.4	Dimethylamine	0	CH_4	0	Ethane	0
N_2H_4	0	H_2	46.3	CO	0.1	Other	0

Average Output Gas Composition:

(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

H_2 70.4 N_2 17.0 CH_4 0 CO 0.2 CO_2 12.4 Ethane 0

% H_2O Used: 33.0 % Reforming to CO_2: 98.4 % to CO: 1.6

Moles NH_3 Formed/Hr: 0.0134 by Keldahl

Moles H_2 per 100 g Aerozine-50 input: 9.30

Moles H_2 per 100 g Total Input: 3.32

Hydrogen Efficiency = 95.0%

AEROZINE-50 STEAM REFORMING DATA SHEET, 1000 HR TEST

System Test No. 5

Notebook Reference No.

Reactor No. after last reactor

Cumulative Time of Catalyst Operation 662 hours

Catalysts 1st G-72 2nd G-56B 3rd G-66B

Temperature, °C 445, 790, 275

Pressure, psig 50, 5, 5

Gas Volume Rate 24.03 l/hr (25°C)

Moles Gas Produced/hr 0.9770

% N_2H_4 Used 100

% UDMH Used 100

	UDMH	H_2O	N_2H_4	Total
Feed Composition, mole-%	6.72	80.67	12.60	100.0
Feed Composition, g/hr	3.630	13.075	3.630	20.335
Feed Composition, mole/hr	0.0605	0.7264	0.1134	0.9003

Total Output Composition, mole-%

UDMH	0	NH_3	0.8	N_2	11.4	CO_2	8.2
H_2O	32.9	Dimethylamine	0	CH_4	0.1	Ethane	0
N_2H_4	0	H_2	46.5	CO	0.1	Other	0

Average Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

H_2 70.1 N_2 17.2 CH_4 6.2 CO 0.2 CO_2 12.3 Ethane 0

% H_2O Used: 33.4 % Reforming to CO_2: 99.3 % to CO: 1.7

Moles NH_3 Formed/Hr: 0.0119 by Keldahl

Moles H_2 per 100 g Aerozine-50 input: 9.43

Moles H_2 per 100 g Total Input: 3.37

Hydrogen Efficiency = 96.4%

AEROZINE-50 STEAM REFORMING DATA SHEET, 1000 HR TEST

System Test No. 6

Notebook Reference No. ______

Reactor No. after last reactor

Cumulative Time of Catalyst Operation 859 hours

Catalysts

	1st	2nd	3rd
Catalysts	G-72	G-56B	G-66B

Temperature, °C 445, 790, 275

Pressure, psig 50, 5, 5

Gas Volume Rate 25.503 l/hr (25°C)

Moles Gas Produced/hr 1.0367

% N_2H_4 Used 100

% UDMH Used 100

	UDMH	H_2O	N_2H_4	Total
Feed Composition, mole-%	6.72	80.67	12.60	100.0
Feed Composition, g/hr	3.849	13.862	3.849	21.560
Feed Composition, mole/hr	0.0641	0.7701	0.1203	0.9545

Total Output Composition, mole-%

UDMH	0	NH_3	0.7	N_2	11.4	CO_2	8.2
H_2O	32.8	Dimethylamine	0	CH_4	0.2	Ethane	0
N_2H_4	0	H_2	46.5	CO	0.2	Other	0

Average Output Gas Composition:

(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

H_2	N_2	CH_4	CO	CO_2	Ethane
69.9	17.2	0.3	0.3	12.3	0

% H_2O Used: 33.5 % Reforming to CO_2: 99.4 % to CO: 2.4

Moles NH_3 Formed/Hr: 0.0114 by Keldahl

Moles H_2 per 100 g Aerozine-50 input: 9.42

Moles H_2 per 100 g Total Input: 3.36

Hydrogen Efficiency = 96.2%

AEROZINE-50 STEAM REFORMING DATA SHEET, 1000 HR TEST

System Test No. 7

Catalysts: 1st G-72, 2nd G-56B, 3rd G-66B

Notebook Reference No. ________

Temperature, °C 445, 790, 275

Reactor No. after last reactor

Pressure, psig 50, 5, 5

Cumulative Time of Catalyst Operation 1000 hours

Gas Volume Rate 23.84 l/hr (25°C)

Moles Gas Produced/hr 0.9691

% N_2H_4 Used 100

% UDMH Used 100

	UDMH	H_2O	N_2H_4	Total
Feed Composition, mole-%	6.72	80.67	12.60	100.0
Feed Composition, g/hr	3.450	12.422	3.450	19.322
Feed Composition, mole/hr	0.057^{5}	0.6901	0.1078	0.8555

Total Output Composition, mole-%

UDMH	0	NH_3	0.7	N_2	11.5	CO_2	7.8
H_2O	33.5	Dimethylamine	0	CH_4	0.2	Ethane	0
N_2H_4	0	H_2	46.1	CO	0.2	Other	0

Average Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

H_2 69.6 N_2 17.7 CH_4 0.3 CO 0.3 CO_2 12.1 Ethane 0

% H_2O Used: 34.4 % Reforming to CO_2: 102.0 % to CO: 2.5

Moles NH_3 Formed/Hr: 0.0126 by Keldahl

Moles H_2 per 100 g Aerozine-50 input: 9.35

Moles H_2 per 100 g Total Input: 3.34

Hydrogen Efficiency = 95.6%

APPENDIX II

COMPUTER PROGRAM FOR CALCULATION OF EQUILIBRIUM STEAM REFORMING PARAMETERS OF AEROZINE-50

```
101. -READY        LOAD(STRFM3)
166. +READY        LIST
101. =       CF    PROGRAM STREFM
102. =             PRINT 1
103. =           10FORMAT(39H ENTER VALUES FOR EQUIL. STEAM REFORM. 52H CONST.,SHIFT
                  1CONST., INPUT, GM ATMS H2, GM ATOMS C,     /  31H GM ATMS O2, GM AT
                  2MS INERT DIA 40H TMC GAS, ELIMR, ELIMS AND TEMP DEG K     /  23H P
                . 4RESS PSIG  XCESS H2O     )
104. =       CF    READ 0,AKR,AKS,AHGA,ACGA,AOGA,ANGA,ELIMR,ELIMS,TEMP,XPSIG,XCESS
105. =             CH41=.011
106. =             CO2=.1
107. =             DCH4=10.
108. =             DCO2=10.
109. =             KK=0
110. =             GO TO 5
111. =           3 KK=KK+1
112. =             ELIMR=ELIMR/2.
113. =             ELIMS=ELIMS/2.
114. =             DCH4=DCH4/10.
115. =             DCO2=DCO2/10.
116. =           5 DO 101 I=1,40
117. =             CH4=CH41
118. =             CO2=CO2+DCO2
119. =             DO 100 J=1,60
120. =             CH4=CH4+DCH4
121. =            0XKR=(ACGA-CO2-CH4)*(.5*AHGA+ACGA+CO2-AOGA-3.*CH4)**3/(CH4*(AOGA+CH
                  44-ACGA-CO2)*(.5*ANGA+ACGA+.5*AHGA-2.*CH4)**2)
122. =             IF(AKR-XKR+ELIMR)100,10,10
123. =          100XKS=CO2*(.5*AHGA+ACGA+CO2-AOGA-3.*CH4)/((ACGA-CO2-CH4)*(CH4+AOGA-A
                  4CGA-CO2))
124. =             IF(AKS-XKS-ELIMS)20,20,101
125. =          20 CONTINUE
126. =             PRINT 15
127. =          15 FORMAT(6X,3HCH4,15X,3HCO2,15X,3HXKR,15X,3HXKS    )
128. =       CF    PRINT 0,CH4,CO2,XKR,XKS
129. =             GO TO 102
130. =         100 CONTINUE
131. =         101 CONTINUE
132. =         102 IF(KK-4)103,110,110
133. =         103 CH41=CH4-DCH4
134. =             CO2=CO2-DCO2
135. =             GO TO 3
136. =         110 CONTINUE
137. =             H2=.5*AHGA+ACGA+CO2-AOGA-3.*CH4
138. =             CO=ACGA-CO2-CH4
139. =             H2O=AOGA+CH4-ACGA-CO2
140. =             XN2=.5*ANGA
141. =             TOT=.5*ANGA+ACGA+.5*AHGA-2.*CH4
142. =             PRINT 120
143. =         120 FORMAT(7X,2HH2,15X,3HXN2,15X,3HCO2,16X,2HCO,15X,3HCH4,15X,3HH2O   )
144. =       CF    PRINT 0,H2,XN2,CO2,CO,CH4,H2O
145. =             H2PC=H2*100./TOT
146. =             XN2PC=XN2*100./TOT
147. =             CO2PC=CO2*100./TOT
148. =             COPC=CO*100./TOT
149. =             CH4PC=CH4*100./TOT
150. =             H2OPC=H2O*100./TOT
151. =             PRINT 130
152. =         130 FORMAT(30X,39HMOLE PERCENT OF EACH SPECIES AT EQUIL.    )

153. =       CF    PRINT 0,H2PC,XN2PC,CO2PC,COPC,CH4PC,H2OPC
154. =             PRINT 135
155. =         1350FORMAT(40HCHECK FO SIGNIFICANCE OF NH3 FORMATION  /58HENTER VALUE
                  4FOR NH3 FORMATION CONST. CORRECTED FOR PRESS.  )
156. =       CF    READ 0,AKNH3
157. =             XNH3=AKNH3*H2**1.5/TOT
158. =             IF(XNH3-1.)136,136,138
159. =         136 PRINT 137
160. =         137 FORMAT(21HNH3 FORMATION INSIGN.  )
161. =             GO TO 140
162. =         138 PRINT 139,XNH3
163. =         139 FORMAT(28HNH3 FORMATION IS SIGNICANT  /  5HXNH3=,F8.3    )
164. =         140 CONTINUE
165. =             END
166. +READY
```

APPENDIX III

PEROXIDE - ACID TITRATION
METHOD FOR DETERMINATION OF N_2O_4

The N_2O_4 gas is bubbled through a 10% H_2O_2 solution made up from 67ml of distilled water and 33ml of 30% H_2O_2 for a measured time. Depending on flow rate, a sample can be collected from 2 to 30 minutes. The peroxide is used to convert the nitric oxides completely to nitric acid, rather than to a mixture of nitric and nitrous acids.

The solution is equilibrated for at least 1 hour (preferably overnight). Then an aliquot is withdrawn and titrated with standard sodium hydroxide solution, using a methyl red plus methylene blue indicator. The end point is observed when the color changes from pink to green (about pH 4-4.5). This indicator is used because the peroxide present in the solution would interfere at higher pH. Since nitric acid is a strong acid, very little error is introduced by taking the end point at pH 4-4.5 instead of pH 7.0.

The grams of N_2O_4/hour are calculated as follows:

$$\text{g } N_2O_4/\text{hour} = \frac{(\text{Ml NaOH})(\text{Normality})}{2} \text{ X } \frac{60 \text{ min/hour}}{\text{minutes to collect sample}} \text{ X } \frac{100\text{ml}}{\text{aliquot withdrawn}} \text{ X } 0.092 \text{ g/millimole } N_2O_4$$

Based on

$$N_2O_4 + N_2O_2 \rightarrow 2HNO_3$$

$$HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$$

Indicator is:

0.1% Methyl red
0.005% Methylene blue
Dissolved in alcohol
Use 5-7 drops for each sample

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