

PROJECT ADMINISTRATION DATA SHEET

ORIGINAL REVISION NO. _____

V. 2637

Project No. E-19-601 GTRI/GIT ~~XXXX~~ DATE 10/15/82

Project Director: Dr. Jack Winnick School/Lab ~~XXXX~~ ChE

Sponsor: NASA - JFK Space Center

Type Agreement: Contract No. NAS10-10560

Award Period: From 10/6/82 To 8/5/83 (Performance) 2/10/84 (Reports) 9/5/83

Sponsor Amount: Total Estimated: \$ 30,145 12-31-83 Funded: \$ 30,145

Cost Sharing Amount: \$ na Cost Sharing No: na

Title: Oxidant Gas Treatment

ADMINISTRATIVE DATA

OCA Contact DENNIS FARMER
~~Linda H. Bowman~~ x4820

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all revision H/1

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SI-PRO-33
JFK Space Center, NASA
Kennedy Space Center, FL 32899
(305) 867-7225

Defense Priority Rating: none Military Security Classification: none

(or) Company/Industrial Proprietary: _____

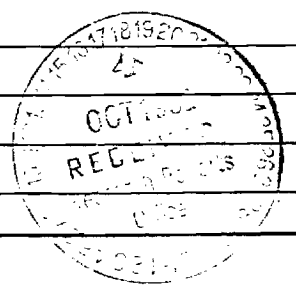
RESTRICTIONS

See Attached na Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval - Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of \$500 or 125% of approved proposal budget category.

Equipment: Title vests with Gov't. If under \$1,000 vests with GIT when prior approval from NASA is obtained.

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SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date 6/12/85

Project No. E-19-601 School ~~OCB~~ ChE

Includes Subproject No.(s) N/A

Project Director(s) Jack Winnick, 1937 GTRC / ~~OCB~~

Sponsor NASA - JFK Space Center

Title Oxidant Gas Treatment

Effective Completion Date: 12/31/83 (Performance) 5/1/84 (Reports)

Grant/Contract Closeout Actions Remaining:

- None
- Final Invoice or Final Fiscal Report Already submitted
- Closing Documents
- Final Report of Inventions already submitted
- Govt. Property Inventory & Related Certificate
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E-1-661

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

SCHOOL OF
CHEMICAL ENGINEERING

February 2, 1983

Ms. Ruth Walker
Contracts Office
Kennedy Space Center
Kennedy Space Center, FL 32899

re: NAS-10-10560

Dear Ms. Walker:

Enclosed are our monthly reports for October through January.
I hope they are the proper format. I will try to assure they are
more prompt in the future.

Sincerely,

Jack Winnick
Professor

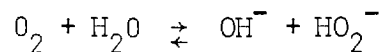
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JW:law

OCTOBER

Objective: Design an Experimental Procedure for Fuel Cell Oxygen Purification

The purification of O_2 using a fuel cell has been done on laboratory scale. The following reaction occurs at the platinum cathode of the fuel cell.



Oxygen will be the only molecule in air that will be reduced. The fuel cell will thus separate O_2 from air, which may be an improvement over distillation. After the cathode reaction occurs the hydroxyl ion migrates through an electrolyte to the nickel oxide anode where the reverse of the cathode reaction occurs, liberating O_2 .

Two experimental fuel cells will be utilized. The first experimental fuel cell will consist of a platinum wire mesh cathode and a nickel oxide wire mesh anode. A solution of potassium hydroxide will be used as the electrolyte. An applied voltage of about 0.5 volts will bias the cell. Once the experiments are started and O_2 is satisfactorily separated from air, technical grade O_2 will be used as an oxidant to see if the cell can further purify it. After this fuel cell is proven a new fuel cell will be built from the materials given to us by United Technologies.

The materials in the second experiment are similar to the materials used in an industrial fuel cell. The anode and cathode are flat discs about three inches in diameter with the metal plated on the top of the discs. An asbestos matrix will be placed between the anode and cathode of the fuel cell. These materials have been donated by United Technologies.

The components will be tightly bolted together using a teflon gasket. The asbestos must be bolted tightly between the anode and cathode so that gas bubbles do not form between the materials. The testing will be similar to the first fuel cell tests.

NOVEMBER

Objective: Catalytic N_2O_4 decomposition literature search

Thermodynamic calculations must first prove that a reaction is possible before considering choice of catalyst. These thermodynamic calculations in Appendix A indicate that the conversion of NO_x to N_2 and O_2 is at least feasible although a catalyst will be needed. N_2O_4 has a temperature dependent equilibrium which lies further to the right with increasing temperature.

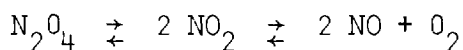


Figure B illustrates this temperature dependent equilibrium which indicates that the catalyst may have to possess properties to decompose a variety of NO_x molecules.

A general reaction can be written for all metals that react with N_2O_4 at low temperatures, which directly relates to catalyst conversion.



This reaction continues to form a nitrosonium salt if the metal is weakly electropositive as zinc on Iron. A catalyst that decomposes N_2O_4 to N_2 and O_2 directly is not feasible at room temperature because the formation (slow) of the salt will deactivate the catalyst and still allow the NO into the air.

By heating the N_2O_4 to form NO_2 and NO via endothermic dissociation, a catalytic bed that can decompose NO_2 and NO to the thermodynamically favored elements of O_2 and N_2 can be considered. The kinetics of the

endothermic dissociation of N_2O_4 are very fast (.001 second) at temperatures over $450^\circ K$.

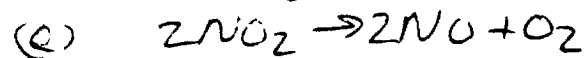
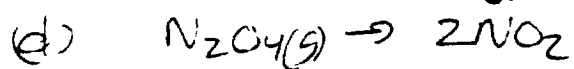
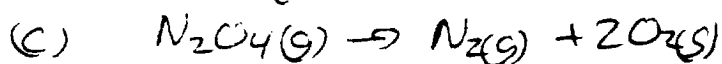
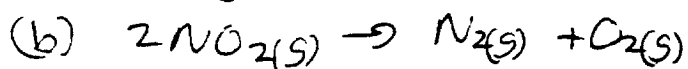
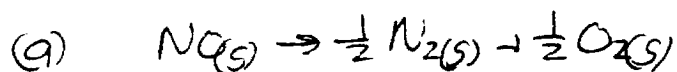
If O_2 desorption from the catalyst is slow, deactivating the catalyst, temperatures close to $773^\circ K$ should be used to keep the catalyst active. At these higher temperatures ($773^\circ K$) O_2 will desorb quickly and the gas will be mainly NO (invisible) and contain about 20% NO_2 (brown), (See Figure B).

In conclusion, a high temperature ($773^\circ K$) catalytic bed will have the best chance of decomposing N_2O_4 .

(2) Calculation of the Enthalpy of Formation of the products in reactions (a), (b), (c), (d) and (e)

Element	ΔH_f° $\frac{\text{kcal}}{\text{mole}}$
$N_2(g)$	0
$O_2(g)$	0
$NO(g)$	21.60
$NO_2(g)$	8.091
$N_2O_4(g)$	2.309

$$\Delta H_{\text{reaction}} = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$$



exothermic

a) $\Delta H_{\text{reaction}} = 0 - 21.60 = -21.6 \frac{\text{kcal}}{\text{mole}} = \Delta H_{\text{reaction}}$

b) $\Delta H_{\text{reaction}} = 0 - 16.182 = -16.182 \frac{\text{kcal}}{\text{mole}} = \Delta H_{\text{reaction}}$

c) $\Delta H_{\text{reaction}} = 0 - 2.309 = -2.309 \frac{\text{kcal}}{\text{mole}} = \Delta H_{\text{reaction}}$

endothermic

d) $\Delta H_{\text{reaction}} = 16.182 - 2.309 = 13.873 \frac{\text{kcal}}{\text{mole}} = \Delta H_{\text{reaction}}$

e) $\Delta H_{\text{reaction}} = (2)(21.6) - 16.182 = 27.018 \frac{\text{kcal}}{\text{mole}} = \Delta H_{\text{reaction}}$

Mole Fraction of the Component
in the Equilibrium Mixture

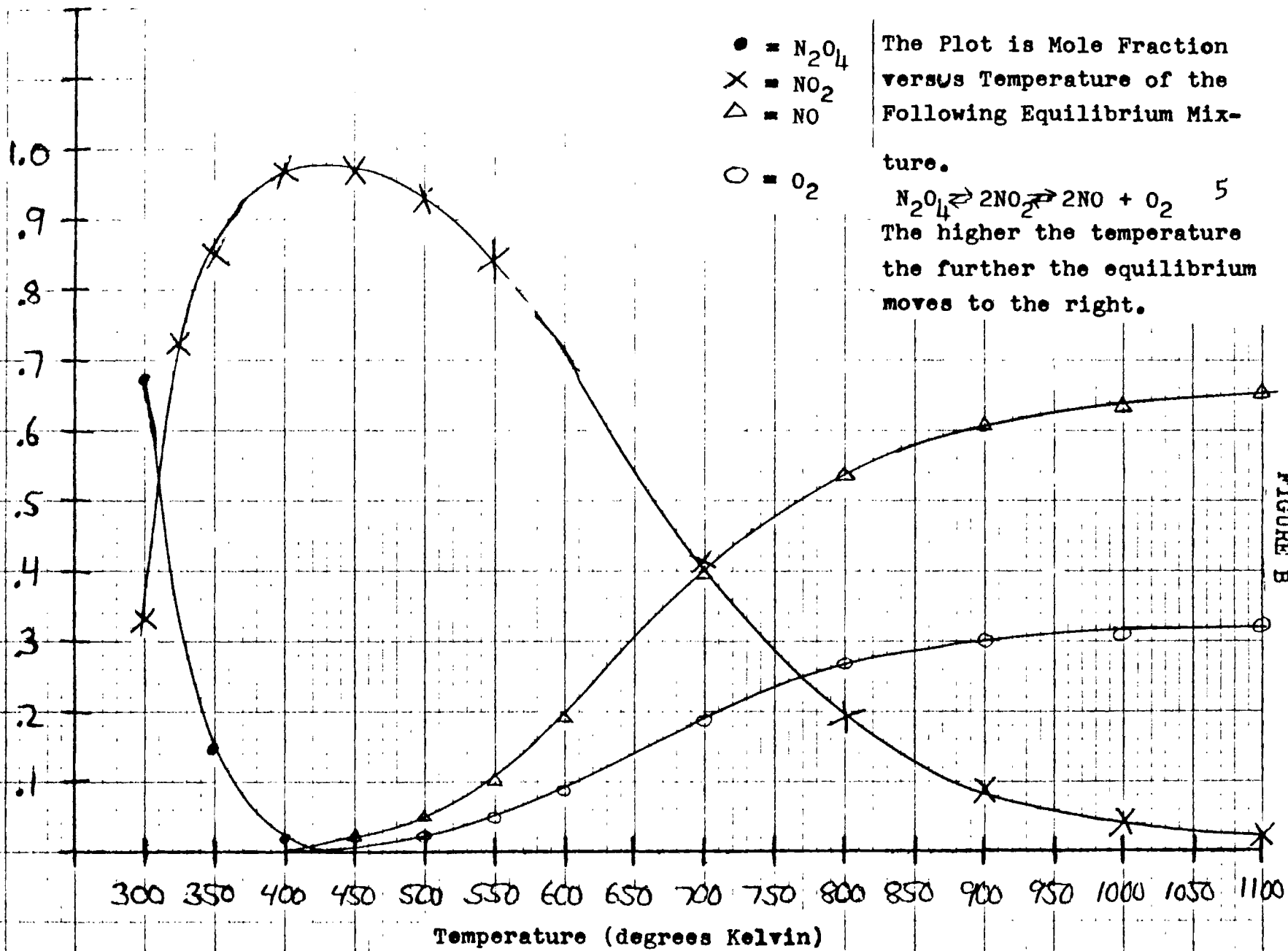
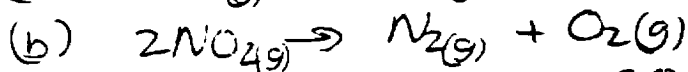
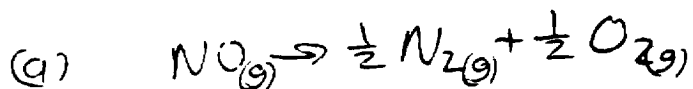


FIGURE B

APPENDIX (A)

(1) Calculation of the Gibbs Free Energy of Formation of Reactions (a), (b) and (c)



Element	ΔG_f° $\frac{\text{kcal}}{\text{mole}}$
$\text{N}_2(g)$	0
$\text{O}_2(g)$	0
$\text{NO}(g)$	20.72
$\text{NO}_2(g)$	12.39
$\text{N}_2\text{O}_4(g)$	23.491

$$\Delta G^\circ_{\text{reaction}} = \Delta G^\circ_{\text{products}} - \Delta G^\circ_{\text{reactants}}$$

$$(a) : \Delta G^\circ_{\text{reaction}} = 0 - 20.72 = -20.72 \frac{\text{kcal}}{\text{mole}} = \Delta G^\circ_{\text{reac}}$$

$$(b) : \Delta G^\circ_{\text{reaction}} = 0 - (2)(12.39) = -24.78 \frac{\text{kcal}}{\text{mole}} = \Delta G^\circ_{\text{reac}}$$

$$(c) : \Delta G^\circ_{\text{reaction}} = 0 - 23.491 = -23.491 \frac{\text{kcal}}{\text{mole}} = \Delta G^\circ_{\text{reac}}$$

$\Delta G^\circ_{\text{reaction}} < 0$ indicates that the reaction is thermodynamically probable. [It can react to form the specified products]

DECEMBER

Objective: Propose experimental procedure for the catalytic decomposition of N_2O_4

The following is a proposed experimental procedure for testing the ability of different catalysts to decompose N_2O_4 .

The experimental apparatus consists of a furnace which surrounds the cylindrical tube that contains the test catalyst. All of the catalysts will be in their oxide form except Pt, which will be supported on Al_2O_3 . The materials are Rh_2O_3 , Co_3O_4 , Pt/ Al_2O_3 , NiO, and Ru_3O_4 . The cylinder holding the catalyst has a length of six inches and an inner diameter of three inches. There will be four iron constantan thermocouples in the four thermowells in the cylinder to measure temperature changes. Two of them will measure the entrance and exit temperatures of the gas and the other two thermocouples will be two and four inches respectively from the gas entrance. The flow of the gases will be horizontal. A Matheson cylinder will hold the N_2O_4 , compressed to five atmospheres so that a driving gas is not needed. If sufficient flow rates are not achieved He will be used to dilute the N_2O_4 and act as a driving gas. The outlet gas stream will be cooled to $100^\circ F$ by having the tubes run through a cold water bath, and then the composition of the mixture will be determined with a suitable detector. The mixture is brought to $100^\circ F$ so that the NO_2 will not react to form NO ¹⁹. At low temperatures this oxidation does not occur¹⁹. The cylinder will be made out of glass which can withstand $700^\circ C$ without deformation. Any stainless steel tubing that the N_2O_4 travels through should be passivated with a (hydrochloric acid, nitric acid) solution to oxidize the Cr in the stainless steel. This is to prevent any N_2O_4 or NO_2 , from reacting with the side walls of the tubing. A large experimental reactor was chosen over a differential

reactor to minimize the amount of error in the results. Some of the N_2O_4 or NO_2 may react with the tubing, however it will be only a small percent of the total flow rate. The main problem area will be at the outlet of the reactor where the temperature is very high. Any distance of stainless steel pipe between the ice bath and the outlet of the reactor must be minimized.

The temperature range of the experiment will be $500^{\circ}K$ to $773^{\circ}K$ unless the results indicate that a higher temperature will be advantageous. Oxygen deactivation of the catalyst below $700^{\circ}K$ will probably be a problem. The conversion levels will be tested at $20^{\circ}K$ intervals for each catalyst. The Matheson cylinder containing the N_2O_4 at approximately five atmospheres will be in a water bath of approximately $80^{\circ}F$. This temperature may be raised because the boiling point of N_2O_4 is $71^{\circ}F$ at one atmosphere. The thermocouples will be zeroed with ice and digital voltmeters will display the temperature readings. A careful pipe and reactor leak check will be made with N_2 before N_2O_4 is let into the system. N_2O_4 is extremely toxic, but even 0.01 ppm can be detected by the human nose. The entire apparatus will be put under a hood and gas masks at hand if needed. After the gases have gone through the detecting device they will go through a calcium hydroxide scrub which then can be disposed. Catalysts may be combined depending on the initial testing. If Co_3O_4 converts all of the NO_2 to NO and none of the NO to $1/2N_2 + 1/2 O_2$ we would fill the top half of the cylinder with $Pt/Al_2O_3^7$ because it decomposes NO to the basic elements and fill the bottom half of the cylinder with Co_3O_4 . This could be a very real possibility. Ragchig rings would be used in the calcium hydroxide scrub with stainless steel pipe and pump. The above is a proposed experimental approach which can be followed at the discretion of the scientists at NASA.

JANUARY

Objective: Catalytic N_2O_4 destruction

A meeting was held at Georgia Tech with Dr. Coleman Bryant of Kennedy Space Center. Details of the experiment at Kennedy Space Center for testing industrial catalysts were discussed. Flow rates and temperatures for the two different types of catalysts were agreed upon. Analytical methods were also agreed on. Testing may begin in February.

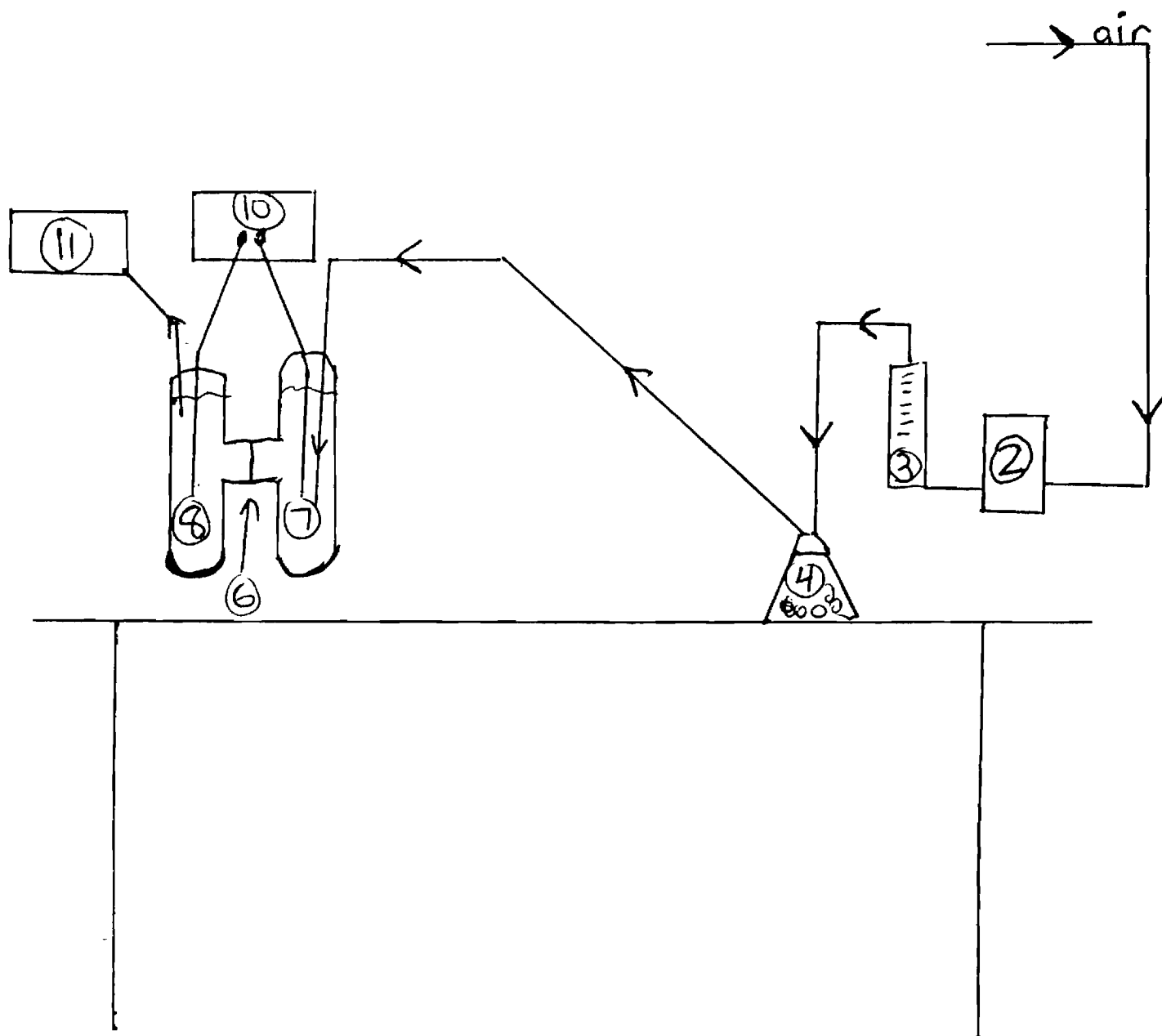
JANUARY

Objective: Set-up experimental fuel cell and examine the economics of the fuel cell

A schematic of the experimental apparatus is shown in Figure A, with the fuel cell scaled up larger than the rest of the equipment. Air will be let in through the regulator (2) and then the rotameter (3), which will allow good control of the air flowrate. The air then passes through the calcium hydroxide scrubber (4) to remove any carbon dioxide. The scrubber consists of a two hundred milliliter erlenmeyer flask packed with raschig rings. The amount of carbon dioxide in the air is usually around 300 ppm, which would be within the experimental error of the rotameter; therefore the small decrease in the flow rate after the air has been scrubbed will not be noticeable. The air then flows to the Pt wire mesh cathode (7) where the cathodic reaction occurs. The air blown to the Pt cathode will travel down through a tube through the electrolyte and will be bubbled on to the cathode using a fritted disc. Good contact between the KOH solution, the gas, and the Pt cathode is necessary for an efficient reaction to occur. The hydroxyl ions then pass through a glass frit (6) and react at the NiO wire mesh anode (8) with the reverse of the cathode reaction. The pure O_2 then leaves and can be collected in a sample flask (11) to be analyzed. The voltage drop across the cell is provided by the voltage supply (10).

The H shaped glass casing which holds the fuel cell, (KOH solution, anode NiO, and cathode Pt) is approximately six inches high and six inches wide with a one-inch inner diameter. Once the experiments are started and O_2 is satisfactorily separated from air, tech. grade O_2 will be used as an oxidant to see if the cell can further purify it. After this fuel cell is proven a new fuel cell will be built from materials given to us by United

FIGURE 8



Technologies.

The main focus of the experiment is to determine the purity of the oxygen product at varying current densities. The size of the current density will be one factor that will decide whether the fuel cell O_2 purification is economically feasible. A voltage versus current plot will be made to find the optimum operating condition. The power costs to purify 10,000 pounds of liquid O_2 is anticipated to be approximately \$240.00, significantly less than a distillation operation (See Appendix B). The cost of the fuel cell is dependent on the current density. If a high current density can be achieved without sacrificing product purity, then a smaller total surface area will be needed and the cost of the cells will decrease. The cost of the fuel cells will ultimately depend on the rate of purification necessary. Appendix B shows that the initial cost of a fuel cell to purify 10,000 pounds every three weeks would be approximately \$60,000.00.

APPENDIX (B)

- (1) Calculation of Current and Power Cost for a Fuel Cell with a 10,000 lb O₂/3 weeks purification rate.
-

$$\frac{\text{week}}{5 \text{ days}} \left(\frac{2 \text{ electrons}}{\text{molecule O}_2} \right) \left(\frac{6.03 \times 10^{23} \text{ molecules}}{\text{gram mole}} \right) \left(\frac{454 \text{ grams}}{\text{lb mole}} \right) \left(\frac{1 \text{ lb mole}}{32 \text{ lb}} \right) \left(\frac{10000 \text{ volt/ hour}}{3600 \text{ sec}} \right) \left(\frac{\text{day}}{8 \text{ hour}} \right) \left(\frac{1 \times 10^{-19} \text{ Coulombs}}{\text{electron}} \right)$$

$$= \underline{39606.7 \text{ Amperes}}$$

$$1 \text{ Ampere} = \frac{\text{Coulomb}}{\text{sec}}$$

$$P=IV = (65)(39606.7) = 19803.35 \text{ Watts} = 19.803 \text{ KW}$$

$$(19.803 \text{ KW}) \left(\frac{8 \text{ hour}}{\text{day}} \right) (15 \text{ days}) \left(\frac{.05 \text{ dollar}}{\text{KW hour}} \right) = \$237.64 = \text{energy cost}$$

$$\underline{\$237.64 = \text{energy cost for each 10000 lb O}_2}$$

- (2) Calculation of surface area of fuel cell

$$\frac{39606.7 \text{ Ampere}}{100 \frac{\text{Amperes}}{\text{ft}^2}} = 396.06 \text{ ft}^2$$

- (3) Cost of a fuel cell with this surface area is approximately \$60,000.

(This cost will decrease with increasing current density).

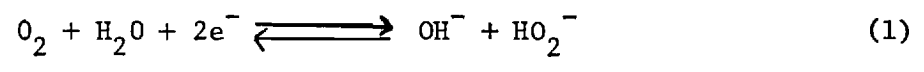
OXIDANT GAS TREATMENT

The purification of Oxygen (O₂) using a fuel cell, and the catalytic decomposition of N₂O₄ will be discussed in this report.

FUEL CELL PURIFICATION OF OXYGEN

THEORY

The purification of O₂ using a fuel cell has been done on laboratory scale. The following reaction occurs at the platinum cathode of the fuel cell.



Oxygen will be the only molecule in air that will be reduced. The fuel cell will thus separate O₂ from air, which may be an improvement over distillation. After the cathode reaction occurs the hydroxyl ions travel through an electrolyte to the nickel oxide anode where the reverse of the cathode reaction occurs, liberating pure O₂ gas. Carbon dioxide must be removed from the gas stream entering the fuel cell with a calcium hydroxide scrub because carbon dioxide will convert the electrolyte to carbonate.

EXPERIMENT #1

The first* experimental fuel cell will consist of a platinum wire mesh cathode and a nickel oxide wire mesh anode. A solution of potassium

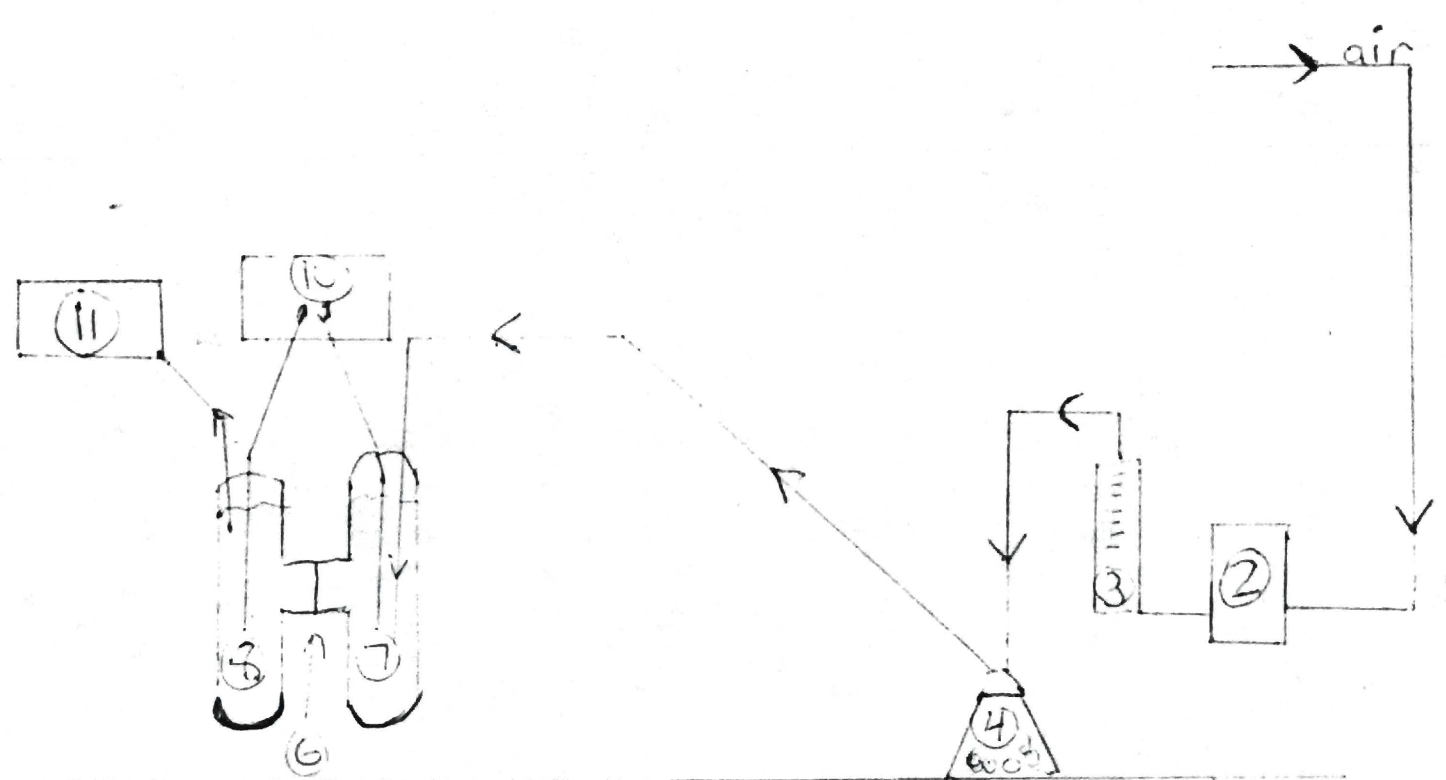
*Both experiments to be performed at Georgia Tech.

hydroxide will be used as the electrolyte. An applied voltage of about 0.5 volts will bias the fuel cell.

A schematic of the experimental apparatus is shown in Figure A, with the fuel cell scaled up larger than the rest of the equipment. Air will be let in through the regulator (2) and then the rotameter (3), which will allow good control of the air flowrate. The air then passes through the calcium hydroxide scrubber (4) to remove any carbon dioxide. The scrubber consists of a two hundred milliliter erlenmeyer flask packed with raschig rings. The amount of carbon dioxide in the air is usually around 300 ppm, which would be within the experimental error of the rotameter; therefore the small decrease in the flow rate after the air has been scrubbed will not be noticeable. The air then flows to the Pt wire mesh cathode (7) where the cathodic reaction occurs. The air blown to the Pt cathode will travel down through a tube through the electrolyte and will be bubbled on to the cathode using a fritted disc. Good contact between the KOH solution, the gas, and the Pt cathode is necessary for an efficient reaction to occur. The hydroxyl ions then pass through a glass frit (6) and react at the NiO wire mesh anode (8) with the reverse of the cathode reaction. The pure O₂ then leaves and can be collected in a sample flask (11) to be analyzed. The voltage drop across the cell is provided by the voltage supply (10).

The H shaped glass casing which holds the fuel cell, (KOH solution, anode NiO, and cathode Pt) is approximately six inches high and six inches wide with a one-inch inner diameter. Once the experiments are started and O₂ is satisfactorily separated from air, tech. grade O₂ will be used as an oxidant to see if the cell can further purify it. After this fuel cell is proven a new fuel cell will be built from materials given to us by United Technologies.

Figure A



EXPERIMENT #2

The materials in the second experiment are similar to the materials used in an industrial fuel cell. The anode and cathode are flat discs about three inches in diameter, with the metal plated on the top of the discs. An asbestos matrix will be placed between the anode and cathode of the fuel cell. These materials have been donated by United Technologies.

The components will be tightly bolted together using a teflon gasket. The asbestos must be bolted tightly between the anode and cathode so that gas bubbles do not form between the materials. The testing will be similar to the first fuel cell tests.

ECONOMICS

The main focus of both of these experiments is to determine the purity of the oxygen product at varying current densities. The size of the current density will be one factor that will decide whether the fuel cell O_2 purification is economically feasible. A voltage versus current plot will be made to find the optimum operating condition. The power costs to purify 10,000 pounds of liquid O_2 is anticipated to be approximately \$240.00, significantly less than a distillation operation (See Appendix B). The cost of the fuel cell is dependent on the current density. If a high current density can be achieved without sacrificing product purity, then a smaller total surface area will be needed and the cost of the cells will decrease. The cost of the fuel cells will ultimately depend on the rate of purification necessary. Appendix B shows that the initial cost of a fuel cell to purify 10,000 pounds every three weeks would be approximately \$60,000.00.

CATALYTIC DECOMPOSITION OF NITROGEN TETROXIDE

The oxidant gas treatment has been researched and recommendations concerning GRACE 701 catalyst², and Co_3O_4 catalyst from Johnson-Mathey

have been sent to NASA. The following is one experimental approach to obtain a catalyst that can decompose N_2O_4 .

THERMODYNAMICS

A thermodynamic calculation must prove that a reaction is possible before considering choice of catalyst. The heats of reaction of $N_2O_4 \longrightarrow 2NO_2$ and of $2NO_2 \longrightarrow 2NO + O_2$ are endothermic (See Appendix A). The heats of reaction of $N_2O_4 \longrightarrow N_2 + 2O_2$, $NO_2 \longrightarrow \frac{1}{2}N_2 + O_2$, and $2NO \longrightarrow N_2 + O_2$ are exothermic and the Gibbs Free Energies of these reactions are negative (See Appendix A). These thermodynamic calculations indicate that the conversion of NO_x to N_2 and O_2 is at least feasible although a catalyst will be needed.

KINETICS

N_2O_4 has a temperature dependent equilibrium which lies further to the right with increasing temperature.^{3,4}

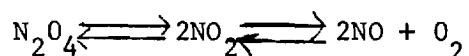
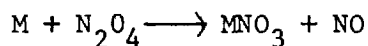


Figure B illustrates this temperature dependent equilibrium.⁵ A general reaction can be written for all metals that react with N_2O_4 at low temperatures, which directly relates to catalyst conversion.^{3,4}



This reaction continues to form a nitrosonium salt if the metal is weakly electropositive as Zinc or Iron.⁵ The reaction may be described as the transfer of an electron from the metal to the dinitrogen tetroxide molecule, yielding the metal ion-nitrate ion pair in place of $NO^+NO_3^-$; the nitric oxide is liberated. The kinetics of the reaction are very slow

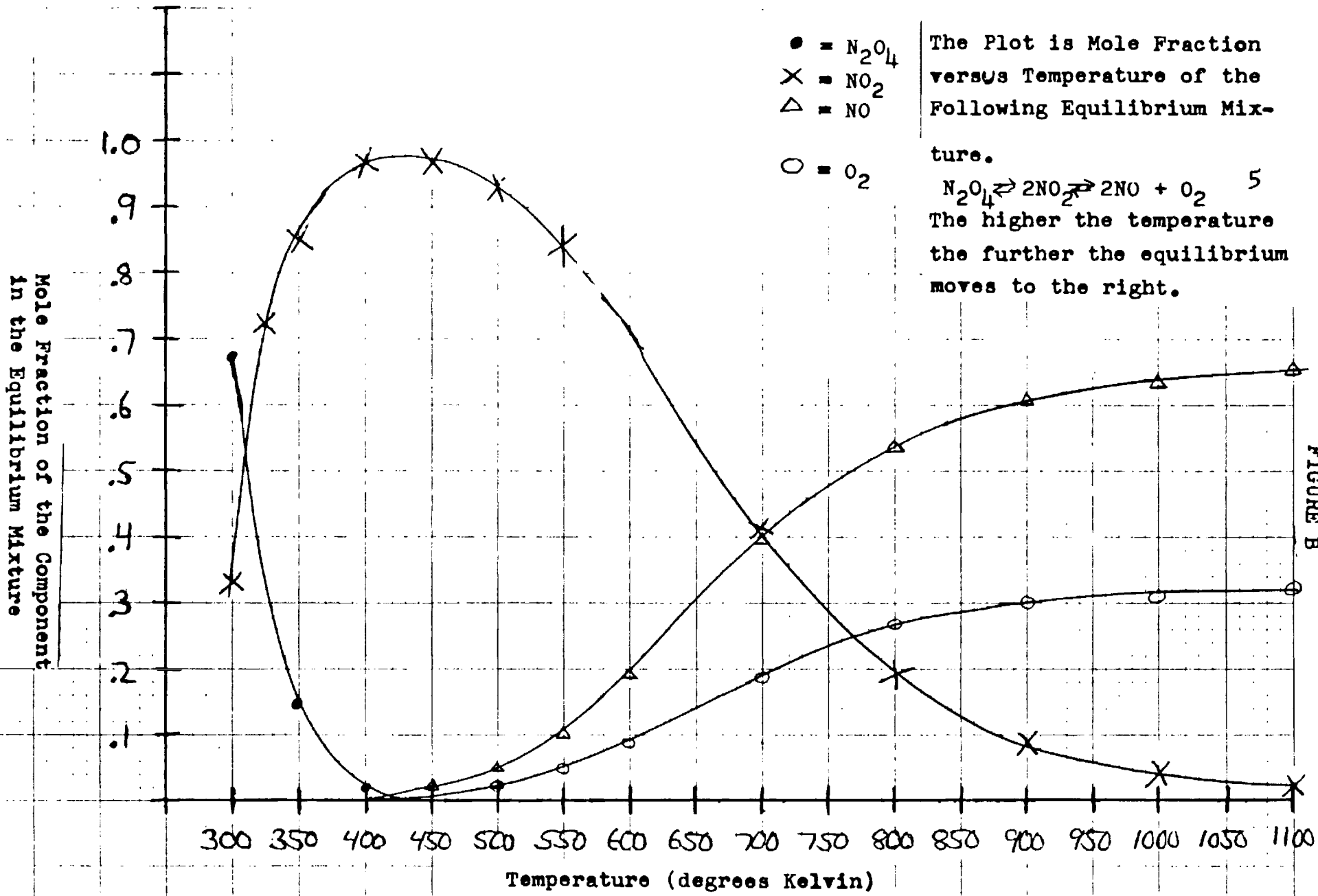


FIGURE B

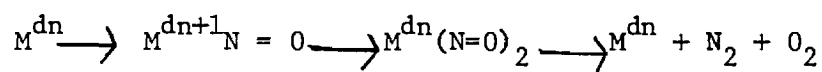
especially when N_2O_4 is in the gaseous state. A catalyst that decomposes N_2O_4 to N_2 and O_2 directly is not feasible at room temperature because the formation (slow) of the salt will deactivate the catalyst and still allow the NO into the air.

By taking advantage of the fact that the N_2O_4 equilibrium mixture becomes essentially NO_2 at temperatures between $400^\circ K$ and $600^\circ K$, a heated catalytic bed that can decompose NO_2 to the thermodynamically favored elements of N_2 and O_2 can be considered. In this temperature range N_2O_4 does not exist but an appreciable amount of NO and O_2 will exist, varying from 1% - 20%.⁵ (See Figure B) The catalyst should then also have the capability of converting NO to the basic elements. Oxygen inhibits the rate of decomposition of NO over Pt,⁹ and oxygen enhances the decomposition rate in quartz vessels.¹⁰ If O_2 desorption from the catalyst is slow, deactivating the catalyst, temperatures close to $773^\circ K$ should be used to keep the catalyst active. At these higher temperatures ($773^\circ K$) O_2 will desorb quickly and the gas will be mainly NO (invisible) and contain about 20% NO_2 (brown), (See Figure B).

The extreme resistance of NO to decomposition is highlighted by an experiment begun in 1918 and continuing to the present time.⁷ Samples of NO were prepared by contacting them with 28 different catalysts, heated to $300^\circ C$ for eight hours then cooled and stored in 1918. The appearance of brown NO_2 would be very sensitive even with the smallest amount of decomposition. In 1957 none⁸ of the samples gave any indication of a brown color and the samples were offered to the Smithsonian Institute for observation in the future.

The¹¹ unusual kinetic stability of NO is due to the fact that the homogeneous, gas phase disproportionation of two NO molecules to N_2

and O_2 is molecular orbital symmetry forbidden. The literature on transition metals shows that the main type of reaction observed when a single gaseous NO molecule reacts with a metal complex is the transfer of the antibonding pi electron, which reduces the metal. The reaction of a second NO molecule with the reduced metal results in an electron transfer to the antibonding orbital of NO. Eisenburg¹³ showed that with Ru the two NO atoms of the nitrosyls were close enough for an interaction to occur which supports the feasibility of the following mechanism.



The three metal oxides which showed the most promise for the above mechanism are Pt/Al₂O₃, Ru₃O₄, and Rh₂O₃,¹¹ which will be included in our experiments.

All of the above mentioned catalysts will decompose NO at high temperatures (> 950°K), to N₂ and O₂, but we propose to work at lower temperatures. In the literature the predominate concern is the decomposition of NO and the decomposition of NO₂ has largely been ignored. This has happened mainly because NO₂ is not a main auto emission pollutant. Two other metal oxides will also be considered as possible catalysts: Co and Ni oxides, are able to react with NO₂ and a reducing gas.¹⁴

The kinetics of the endothermic decomposition of N₂O₄ are important as the residence time of the gas in the catalytic bed will be of the order of a few minutes at the most. As Davidson has shown¹⁵ the endothermic decomposition of N₂O₄ → 2NO₂ occurs in microseconds. The rate constant $k = 10^{16} \exp(-13000/RT) \text{sec}^{-1}$ is for the predicted first order kinetics for the dissociation of N₂O₄. The rate constant becomes second order and decreases when other gases such as NO, N₂, and O₂ are¹⁵ present but the order of magnitude does not change significantly enough for the kinetics of dissociation to become a problem. The endothermic dissociation of

$2\text{NO}_2 \longrightarrow 2\text{NO} + \text{O}_2$ does not have rate limitations as described by Wise¹⁶ at temperatures ($> 600^\circ\text{K}$). The rate of the dissociation is second order with respect to NO_2 and proceeds normally when other gases like NO , O_2 , and N_2 are present. The rate constant for the reaction can be represented by¹⁶ $k = 10^{12.6} \exp(-26,900/\text{RT}) \text{cc/mole/sec}$. At 700°K the endothermic dissociation of $\text{N}_2\text{O}_4 \longrightarrow 2\text{NO}_2$ and $2\text{NO}_2 \longrightarrow 2\text{NO} + \text{O}_2$ will be of the order of microseconds and seconds respectively so the kinetics of the endothermic dissociation of N_2O_4 will not be a problem.

EXPERIMENTAL^{*}

The experimental apparatus consists of a furnace which surrounds the cylindrical tube that contains the test catalyst. All of the catalysts will be in their oxide form except Pt, which will be supported on Al_2O_3 . The materials are Rh_2O_3 , Co_3O_4 , $\text{Pt}/\text{Al}_2\text{O}_3$, NiO , and Ru_3O_4 . The cylinder holding the catalyst has a length of six inches and an inner diameter of three inches. There will be four iron constantan thermocouples in the four thermowells in the cylinder to measure temperature changes. Two of them will measure the entrance and exit temperatures of the gas and the other two thermocouples will be two and four inches respectively from the gas entrance. The flow of the gases will be horizontal. A Matheson cylinder will hold the N_2O_4 , compressed to five atmospheres so that a driving gas is not needed. If sufficient flow rates are not achieved He will be used to dilute the N_2O_4 and act as a driving gas. The outlet gas stream will be cooled to 100°F by having the tubes run through a cold water bath, and then the composition of the mixture will be determined with a suitable detector. The mixture is brought to 100°F so that the NO_2 will not react to form NO ¹⁹. At low temperatures this oxidation does not occur¹⁹. The cylinder will be

^{*}To be performed at KSC

made out of glass which can withstand 700°C without deformation. Any stainless steel tubing that the N_2O_4 travels through should be passivated with a (hydrochloric acid, nitric acid) solution to oxidize the Cr in the stainless steel. This is to prevent any N_2O_4 or NO_2 , from reacting with the side walls of the tubing. A large experimental reactor was chosen over a differential reactor to minimize the amount of error in the results. Some of the N_2O_4 or NO_2 may react with the tubing, however it will be only a small percent of the total flow rate. The main problem area will be at the outlet of the reactor where the temperature is very high. Any distance of stainless steel pipe between the ice bath and the outlet of the reactor must be minimized.

The temperature range of the experiment will be 500°K to 773°K unless the results indicate that a higher temperature will be advantageous. Oxygen deactivation of the catalyst below 700°K will probably be a problem. The conversion levels will be tested at 20°K intervals for each catalyst. The Matheson cylinder containing the N_2O_4 at approximately five atmospheres will be in a water bath of approximately 80°F . This temperature may be raised because the boiling point of N_2O_4 is 71°F at one atmosphere. The thermocouples will be zeroed with ice and digital voltmeters will display the temperature readings. A careful pipe and reactor leak check will be made with N_2 before N_2O_4 is let into the system. N_2O_4 is extremely toxic, but even 0.01 ppm can be detected by the human nose. The entire apparatus will be put under a hood and gas masks at hand if needed. After the gases have gone through the detecting device they will go through a calcium hydroxide scrub which then can be disposed. Catalysts may be combined depending on the initial testing. If Co_3O_4 converts all of the NO_2 to NO and none of the NO to $\frac{1}{2}\text{N}_2 + \frac{1}{2}\text{O}_2$ we would fill the top half of the cylinder

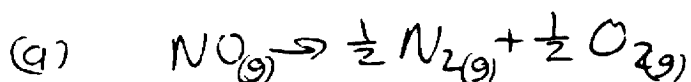
with Pt/Al₂O₃⁷ because it decomposes NO to the basic elements and fill the bottom half of the cylinder with Co₃O₄. This could be a very real possibility. Ragchig rings would be used in the calcium hydroxide scrub with stainless steel pipe and pump. The above is a proposed experimental approach which can be followed at the discretion of the scientists at NASA.

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APPENDIX (A)

(1) Calculation of the Gibbs Free Energy of Formation of Reactions (a), (b) and (c)



<u>Element</u>	<u>ΔG_f°</u>	<u>$\frac{\text{kcal}}{\text{mole}}$</u>
$\text{N}_2(g)$	0	
$\text{O}_2(g)$	0	
$\text{NO}(g)$	20.72	
$\text{NO}_2(g)$	12.39	
$\text{N}_2\text{O}_4(g)$	23.491	

$$\Delta G^\circ_{\text{reaction}} = \Delta G^\circ_{\text{products}} - \Delta G^\circ_{\text{reactants}}$$

$$(a) \quad \Delta G^\circ_{\text{reaction}} = 0 - 20.72 = -20.72 \frac{\text{kcal}}{\text{mole}} = \Delta G^\circ_{\text{react}}$$

$$(b) \quad \Delta G^\circ_{\text{reaction}} = 0 - (2)(12.39) = -24.78 \frac{\text{kcal}}{\text{mole}} = \Delta G^\circ_{\text{react}}$$

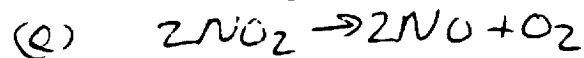
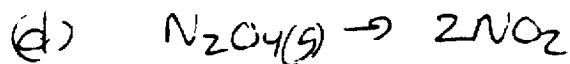
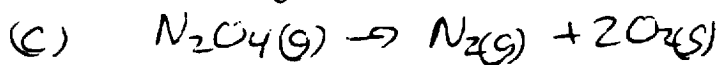
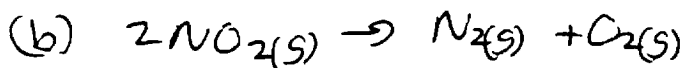
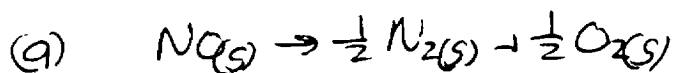
$$(c) \quad \Delta G^\circ_{\text{reaction}} = 0 - 23.491 = -23.491 \frac{\text{kcal}}{\text{mole}} = \Delta G^\circ_{\text{react}}$$

$\Delta G^\circ_{\text{reaction}} < 0$ indicates that the reaction is thermodynamically probable. [It can react to form the specified products]

(2) Calculation of the Enthalpy of Formation
of the products in reactions (a), (b), (c), (d) and (e)

Element	ΔH_f° $\frac{\text{Kcal}}{\text{mole}}$
$\text{N}_2(\text{s})$	0
$\text{O}_2(\text{g})$	0
$\text{NO}(\text{g})$	21.60
$\text{NO}_2(\text{g})$	8.091
$\text{N}_2\text{O}_4(\text{g})$	2.309

$$\Delta H_{\text{reaction}} = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$$



exothermic

(a) $\Delta H_{\text{reaction}} = 0 - 21.60 = -21.6 \frac{\text{Kcal}}{\text{mole}} = \Delta H_{\text{reaction}}$

(b) $\Delta H_{\text{reaction}} = 0 - 16.182 = -16.182 \frac{\text{Kcal}}{\text{mole}} = \Delta H_{\text{reaction}}$

(c) $\Delta H_{\text{reaction}} = 0 - 2.309 = -2.309 \frac{\text{Kcal}}{\text{mole}} = \Delta H_{\text{reaction}}$

endothermic

(d) $\Delta H_{\text{reaction}} = 16.182 - 2.309 = 13.873 \frac{\text{Kcal}}{\text{mole}} = \Delta H_{\text{reaction}}$

(e) $\Delta H_{\text{reaction}} = (2)(21.6) - 16.182 = 27.018 \frac{\text{Kcal}}{\text{mole}} = \Delta H_{\text{reaction}}$

APPENDIX (B)

(1) Calculation of Current and Power Cost for a Fuel Cell
with a 10,000 lb O₂/week purification rate.

$$\frac{\text{week}}{5 \text{ days}} \left(\frac{2 \text{ electrons}}{\text{molecule O}_2} \right) \left(\frac{6.03 \times 10^{23} \text{ molecules}}{\text{gram mole}} \right) \left(\frac{454 \text{ grams}}{\text{lb mole}} \right) \left(\frac{1 \text{ lb mole}}{32 \text{ lb}} \right) \left(\frac{10000 \text{ lb}}{3 \text{ weeks}} \right) \left(\frac{1 \text{ hour}}{3600 \text{ sec}} \right) \left(\frac{\text{day}}{8 \text{ hour}} \right) \left(\frac{1 \times 10^{-19} \text{ Coulombs}}{\text{electron}} \right)$$

$$= \underline{39606.7 \text{ Amperes}}$$

$$1 \text{ Ampere} = \frac{\text{Coulomb}}{\text{sec}}$$

$$P = IV = (65)(39606.7) = 19803.35 \text{ Watts} = 19.803 \text{ KW}$$

$$(19.803 \text{ KW}) \left(\frac{8 \text{ hour}}{\text{day}} \right) (15 \text{ days}) \left(\frac{.05 \text{ dollars}}{\text{KWhour}} \right) = \$237.61 = \text{energy COST}$$

$$\underline{\$237.61 = \text{energy cost for each 10000 lb O}_2}$$

(2) Calculation of surface area of fuel cell

$$\frac{39606.7 \text{ Ampere}}{100 \frac{\text{Amperes}}{\text{ft}^2}} = 396.06 \text{ ft}^2$$

(3) Cost of a fuel cell with this surface area is approximately \$60,000. If a high current density is desirable, the cost of the cell decreases.

with increasing

if we can get the current

density. ~~higher~~

FINAL REPORT

The Space Shuttles that are launched at the Kennedy Space Center in Florida have on board oxygen-hydrogen fuel cells. These fuel cells are used as a power supply or back-up power supply for most systems on the space shuttle. The oxygen that flows by the cathode in these fuel cells must be extremely pure (99.989%).

Purified oxygen is necessary for the fuel cells for two reasons. The first is to prevent accumulation of inert gases such as argon, krypton, and nitrogen. The activation of the cell is decreased because the active surface of the cathode is occupied by the inert gas, preventing the oxygen from reaching the active area. Since the fuel cell operates at total consumption of oxygen, there is no exhaust. This inert gas accumulation eventually causes the power output of the fuel cell to drop to zero because oxygen cannot react at the cathode.

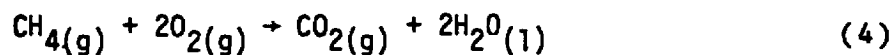
The second reason that pure oxygen is needed for the fuel-cells on the space shuttle is that the concentration of CO_2 , CO and CH_4 in the oxygen feed must be at a minimum. CO_2 will react with the hydroxyl ion in the potassium hydroxide electrolyte to form bicarbonate ion.



Since the electrolyte has a high pH the bicarbonate ion will immediately react to form potassium bicarbonate and precipitate.



The precipitated potassium bicarbonate deactivates the cathode by depositing on the active sites in the catalytic pores. The concentration of CO and CH₄ also needs to be minimized because CO and CH₄ will be oxidized to form CO₂ at the cathode and the previous sequence of reactions will occur.



NASA at the Kennedy Space Center now obtains 99.989% liquid oxygen by purchasing it from private industry. There are storage problems because of the hot weather, especially during the summer months. When liquid oxygen evaporates, in the storage tanks, krypton and methane will not evaporate with the oxygen and will remain in the liquid phase because

they have higher boiling points than oxygen. The storage tanks need to be vented periodically to relieve the pressure inside the tanks. The gas leaving the tank is oxygen and impurities with higher boiling points than oxygen will remain liquid or solid. After each venting the concentration of impurities in the liquid oxygen will increase, because oxygen has left the liquid phase and the impurities have not. Repetitive venting of the storage tank eventually leads to sub-standard oxygen purity.

NASA at the Kennedy Space Center is seeking a technique for on-site production of fuel-cell-grade oxygen to become independent of the supplier and minimize the storage time of the liquid oxygen. The cryogenic distillation of air to obtain 99.989% oxygen is expensive because the boiling points of argon and oxygen are so close, -185.7° C and -182.9° C respectively. Hydrolysis and electrochemical concentration are being considered as practical alternatives.

THEORY

Thermodynamics

The two half cell reactions which occur in the oxygen concentration cell are shown by equations (5) and (6). The reaction at the cathode is exothermic (-79kcal/(grammole of O₂); therefore the cathode will be at a higher temperature than the anode while the cell is operating. The theoretical voltage bias needed to operate the concentrator cell is calculated using the Nernst equation and depends only on the partial pressures of oxygen at the anode and cathode. When breathing air is the feed gas, the partial pressure of oxygen at the cathode is 0.21 atmospheres while the partial pressure of oxygen at the anode is 1.0 atmosphere. The theoretical voltage needed to bias the cell at equilibrium (zero current) can now be calculated using the following equation.

$$(E-E^{\circ}) = \frac{RT}{nF} \ln \left(\frac{P_{O_2}(\text{anode})}{P_{O_2}(\text{cathode})} \right) \quad (7)$$

For the four electron reaction mechanism presented in equations (5) and (6), the calculated theoretical voltage is 0.01 volts. The theoretical voltage when propellant-grade oxygen flows by the cathode is approximately zero at

equilibrium conditions. Because the overall reaction occurring at the cathode is the reverse of the anode, one would expect that the voltage needed to bias the cell would be small. Only the oxygen pressure difference on each side of the cell would constitute a need for voltage bias at equilibrium. The actual voltage needed to bias the cell is two orders of magnitude greater than the theoretical open-circuit voltage because of the internal resistance of the concentrator cell as well as the diffusion and activation limitations under current flow.

Polarization

Upon application of a potential, with the subsequent flow of current, polarization occurs at the electrode and in the bulk electrolyte. Figure 2 shows the potential distribution between the two electrodes under load. The ohmic and electrode overpotentials are also shown in Figure 2.

The potential drop in a cell is called an overpotential [1] which is the difference between the equilibrium or open-circuit voltage of the cell and the actual voltage of an operating cell

$$\eta = E - E_e \quad (8)$$

The overpotential is caused by three kinds of polarization;

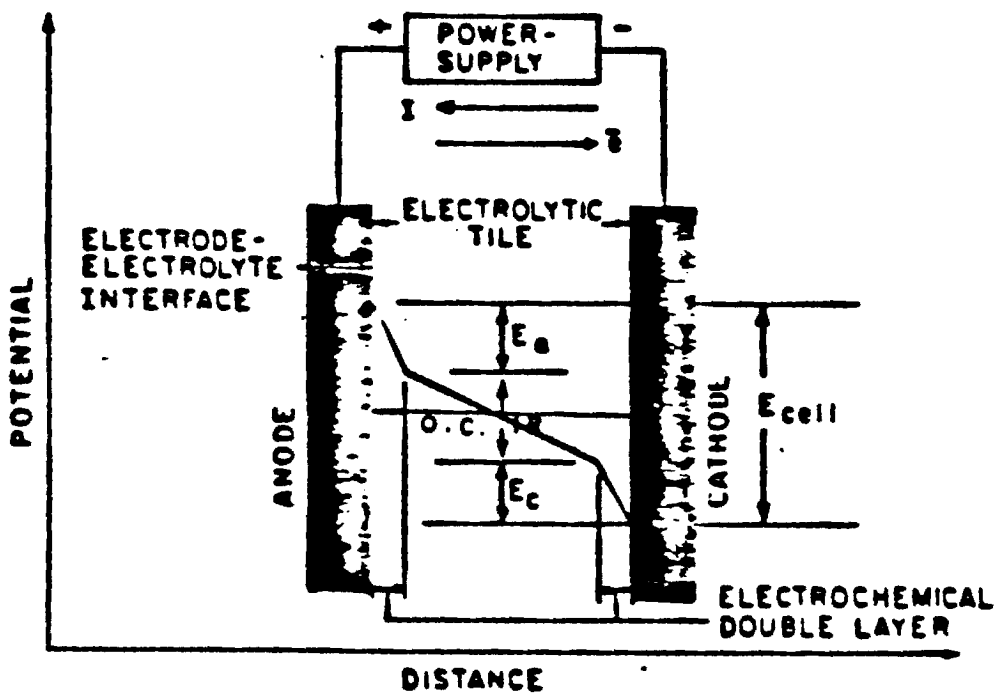


Figure 2 Schematic Representation of Potential Gradient of a Concentration Cell in Driven Mode.

ohmic, activation, and concentration.

$$\eta = \eta_{\text{ohmic}} + \eta_{\text{activation}} + \eta_{\text{concentration}} \quad (9)$$

The total overpotential for an operating cell is

$$\eta_o = -\eta_{\text{cathode}} + \eta_{\text{anode}} \quad (10)$$

where the cathodic overpotential which is negative and anodic overpotential which is positive each have activation, concentration and ohmic contributions. The ohmic overpotential is caused by the direct IR loss of the cell, where R is the impedance of the electrodes, electrolyte and matrix. The activation overpotential is caused by the electrode kinetic rate limitations; the concentration overpotential is caused by the reactant and product diffusion limitations to and from the electrodes.

Ohmic

Ohmic losses cause the potential drop developed when the polarizing current I overcomes the resistance of the electrolyte.

$$R = \frac{I}{rA} \quad (11)$$

The resistance of the concentrator cell is minimized by

using a high-conductivity electrolyte and minimizing the distance between the anode and cathode by using a very thin asbestos matrix. The concentration gradient of the cell then becomes large because of the shorter distance. Metallic oxides also contribute to the ohmic resistance, therefore the ohmic resistance will vary from cell to cell depending on construction and the amount of metallic oxide present on current collectors and electrodes. The current flowing through the ohmic resistance decays much faster than the other overpotentials; therefore, a current interruption [42] technique utilizing an oscilloscope and a potentiostat can be implemented to measure it.

Activation

When diffusion effects at the electrodes are negligible the following form of Butler-Volmer equation can be used to describe the kinetics of the reaction at an electrode. (Bockris and Reddy, 1970)

$$I = I_0 \left(\exp \left[\frac{\alpha F \eta}{RT} \right] - \exp \left[\frac{-\alpha F \eta}{RT} \right] \right) \quad (12)$$

The Butler-Volmer equation has an anodic and cathodic contribution to the current density (I).

The equilibrium exchange current density (I_0) represents the individual electronation and de-electronation

currents underlying the state of equilibrium of the cell. Exchange current densities vary from one reaction to another and from one electrode material to another by many orders of magnitude, because they reflect the kinetic properties of the interfacial system concerned.

An equilibrium exchange current implies that the net exchange of electrons across the electrode interface is zero. The overpotential is represented by (η) and the transfer coefficients by ($\alpha^<$ and $\alpha^>$). One set of parameters ($\alpha^<, \alpha^>, I_0$) incorporated in Equation (12) describe the kinetics at the anode while another set of parameters ($\alpha^<', \alpha^>', I_0'$) placed in Equation (12) describe the kinetics at the cathode. If $I_0 = I_0'$ then only one set of parameters incorporated into Equation (12) is needed to characterize the kinetics of both electrodes because $\alpha^< = \alpha^<'$ and $\alpha^> = \alpha^>'$. This implies the reaction mechanism is the same at the anode and cathode. $I_0 \neq I_0'$ for the oxygen concentrator cell; therefore two sets of parameters are needed to describe the reaction kinetics and the reaction mechanism at the anode and cathode are not identical.

The anodic and cathodic transfer coefficients at each electrode have the following relationship

$$\alpha^< + \alpha^> = \frac{N}{V} \quad (12a)$$

where (N) is the total number of electrons that are

transferred and the number of times the rate limiting step occurs is designated as (V) . Note that the anodic and cathodic transfer coefficients at the cathode are not necessarily equal to the anodic and cathodic transfer coefficients at the anode.

Tafel Region

The Butler-Volmer equation (12), reduces to the Tafel form when the cathodic or anodic contribution is less than 1.0% of the total current. This occurs at overpotentials greater than 100 mV or less than -100 mV. The Tafel forms of the Butler-Volmer equation (12) when the cathodic or anodic contribution is negligible follow.

$$\eta > 100\text{mV}$$

$$\ln(I) = \ln(I_0) + \frac{\alpha F \eta}{RT} \quad (13)$$

$$\eta < -100\text{mV}$$

$$\ln(I) = \ln(I'_0) - \frac{\alpha' F \eta}{RT} \quad (14)$$

Note that when $\ln(I)$ versus η is plotted the intercept at the ordinate when $\eta = 0$ is $\ln(I_0)$. The Tafel slope is the slope of the line $\left(\frac{\alpha F}{RT}\right)$. The exchange current density (I_0) and a transfer coefficient (α) for the anode and cathode can be determined from the slopes and intercepts of Tafel plots. Equation (13) allows the (I_0) and (α) to be determined for the anode, while Equation (14) allows the (I'_0) and (α') to

be determined for the cathode.

Diffusion .

The diffusional or concentration overpotential when migration and convection effects are negligible is expressed by (Bockris and Reddy, 1970) using the Nernst equation.

$$\eta_{\text{concentration}} = \frac{RT}{nF} \ln \frac{C_{x=0}}{C^{\circ}} \quad (15)$$

where $C_{x=0}$ is the concentration of the limiting reactant at the reaction site and C° is the concentration of the limiting reactant in the bulk phase of the feed gas. The electronation or de-electronation current density is described using Fick's First Law of Diffusion.

$$J_D = D \frac{dC}{dx} \quad (16)$$

where the flux term J_D can be expressed as

$$\frac{I}{nF} = J_D \quad (17)$$

since the current density is proportional to the molar flux (J_D). Equation (17) substituted into equation (16) gives the following if a linear concentration gradient is assumed,

$$I = nFD \frac{(C^\circ - C_{x=0})}{\delta} \quad (18)$$

where δ is the effective diffusion layer thickness. As the bias over the electrode is increased, the current density will increase and the concentration of the limiting reactant at the surface of the electrode will approach zero. When the concentration of the limiting reactant at the surface of the electrode reaches zero, the current density is at a maximum and is called the limiting current density as shown below.

$$\frac{I_1}{nF} = J_D \quad (19)$$

Substituting equation (19) and (18) into equation (15) and rearranging, the diffusion overpotential becomes

$$\eta_{\text{concentration}} = \frac{RT}{nF} \ln \left(1 - \frac{I}{I_1} \right) \quad (20)$$

Cathode Mathematical Model

A mathematical model for correlating the cathode performance with scrubbed breathing air is considered here. If the reaction kinetics (activation-controlled current overpotential relationship) can be represented by the Butler-Volmer equation (12) an expression for mixed control

(activation and diffusion) can be represented by a modified Butler-Volmer equation [1].

$$I = I_0 \left(\frac{C_{p,x=0}}{C_p^0} \exp \frac{\alpha F \eta}{RT} - \frac{C_{R,x=0}}{C_R^0} \exp \frac{\zeta F \eta}{RT} \right) \quad (21)$$

$\frac{C_{i,x=0}}{C_i^0}$ is the ratio the limiting species' concentration at the electrode to its concentration in the bulk phase, where the subscript p represents the product and the subscript R represents the reactant. As shown earlier $\frac{C_{i,x=0}}{C_i^0}$ is related to current.

The ratio $\frac{C_{i,x=0}}{C_i^0}$ is determined by considering the zones of gaseous diffusion. In the first zone (flow cavity) the molar flux is described by the following equation,

$$J_D = \frac{I}{nF} = -kg (C^0 - C^*) \quad (22)$$

where C^* is the concentration of oxygen at the entrance of the pore. C^0 is the concentration of oxygen in the bulk feed gas. In the second zone (the pore) the molar flux is represented by the following equation,

$$J_D = \frac{I}{nF} = -D_{\text{eff}} \frac{(C^* - C_{x=0})}{\delta_g} \quad (23)$$

where $C_{x=0}$ is the concentration of oxygen at the three phase reaction site. δ_g is the diffusional boundary layer

thickness. The effective diffusivity is defined as follows:

$$D_{\text{eff}} = D_{AB} \frac{\epsilon}{\tau} \quad (24)$$

where τ is the tortuosity, ϵ the void fraction of the electrode, and D_{AB} the gaseous binary diffusivity. Since the flux in the cavity is equal to the flux in the pore, C^* can be eliminated when combining Equations (22) and (23) to give.

$$\frac{C_{r,x=0}}{C_R} = 1 + \frac{I}{nFC^0} \left(\frac{1}{kg} + \frac{\tau \delta g}{D_{AB}\epsilon} \right) \quad (25)$$

The limiting current when $C_{r,x=0}$ equals zero is

$$I_L = -nFC^0 / \left(\frac{1}{kg} + \frac{\tau \delta g}{D_{AB}\epsilon} \right) \quad (26)$$

Equation (21) takes the Tafel form

$$I = -I_0 \left(1 - \frac{I}{I_L} \right) \exp \frac{-\alpha' F \eta}{RT} \quad (27)$$

and the tortuosity (τ), the exchange current density (I_0') and the cathodic transfer coefficient (α') can be allowed to

be parameters which are varied to give the best fit to the data.

Mass transfer coefficients (k_g) for laminar flow over a flat plate can be predicated with the following equations [45].

$$(N_{sh})_{lm} = \frac{k_g L}{D_{AB}} = 0.646 N_{Re,L}^{1/2} N_{Sc}^{1/3} \quad (28)$$

The length of the flow channel is taken to be 6.8 cm because of the irregular Exmet material, and the velocity of the gas is given by

$$V = Q/A_{cs} \quad (29)$$

where the cross sectional area (A_{cs}) of the flow channel is 1.9 cm². Binary diffusivities for gases can be predicted with the following equation [45].

$$D_{AB} = 0.001 T^{7/4} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2} / P \left(\left[(V)_A^{1/3} + (V)_B^{1/3} \right]^2 \right) \quad (30)$$

V is the atomic diffusion volume increments to be summed for each component, T is the temperature of the gas in degrees Kelvin, M the molecular weight, and P is the pressure of the gas in atmospheres. δ_g is taken to be the electrode thickness (0.034 cm) and ϵ is estimated at 0.5.

CONCLUSIONS

The concept of electrochemical gas concentration has been tested as a means for producing oxygen of sufficient quality for use as oxidant in alkaline fuel cells. A laboratory-scale cell was assembled using state-of-the-art components. Electrochemical design parameters were obtained with both breathing-air and propellant-oxygen feed. Purities of evolved oxygen exceeded the quality criterion for fuel-cell use. An economic analysis indicates the method is highly attractive as a means for on-site high-purity oxygen production.