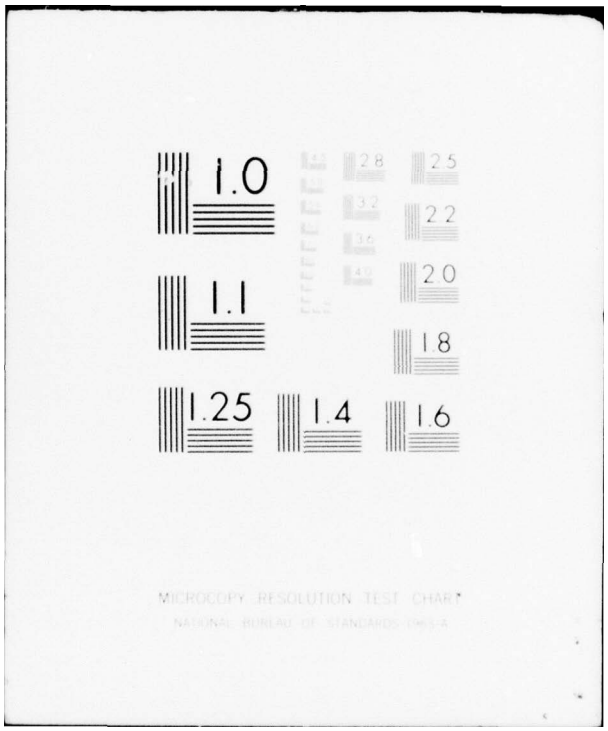
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CHEMICAL GENERATION OF GASEOUS EXCITED OXYGEN

Quantum Institute
University of California
Santa Barbara, CA 93106

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August 1977

Final Report

Approved for public release; distribution unlimited.

AIR FORCE WEAPONS LABORATORY
Air Force Systems Command
Kirtland Air Force Base, NM 87117

This final report was prepared by Quantum Institute, Department of Physics, at the University of California, Santa Barbara, California, under Contract F29601-75-C-0058, Job Order 33260308, with the Air Force Weapons Laboratory, Kirtland Air Force Base, New Mexico. Major Bousek (ALC) was the Laboratory Project Officer-in-Charge.

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The object of the work was to design, build, and test a chemical generator to produce a high yield of electronically excited oxygen molecules, O_2 ($^1\Delta$). The generator is needed as a laboratory tool and as a model for scaling future apparatus to produce larger outputs. The work is divided into three parts. In Part One, the candidate chemical reaction was chosen, the chemical generator and necessary output measuring devices were designed and built, and preliminary data were obtained. The second part was a study of the effects of systematic changes in operating parameters on the performance of the generator

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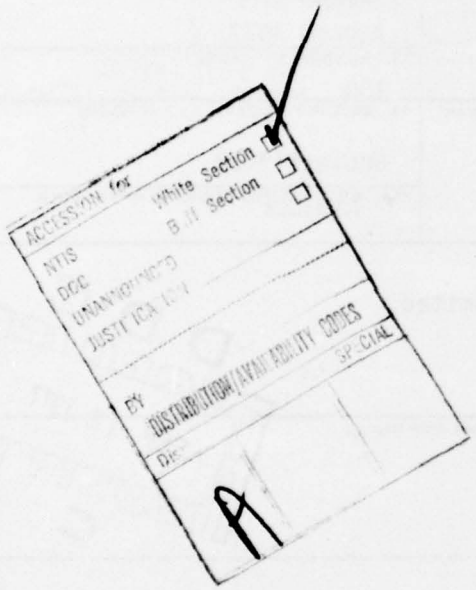
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The third part was a consolidation of the results obtained from Part Two into modifications and improvements of the generator with the objective of maximizing the $O_2^{\uparrow}$ ~~$(^1\Delta)/O_2(^3\Sigma)$~~ yield. The reaction scheme consisted of the condensation of a halogen (bromine or chlorine) on a rotating dewar, followed by reaction with a basic hydrogen peroxide solution. The rotating dewar is then scraped clean for re-deposition of fresh halogen, allowing the generator to run continuously for long periods of time (~45 minutes, typically). The highest yield was obtained using chlorine and 90% H_2O_2 (with 15% NaOH by weight), giving $O_2(^1\Delta)/O_2(^3\Sigma) \approx 24\%$. Fast-flow cryogenic trapping removed all of the impurities except for excess chlorine, an undetermined amount of which was present in the output flow.



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ABBREVIATIONS AND SYMBOLS

I_{Sat}	saturation current
I_{Std}^{40}	irradiance of standard lamp at 40 cm
L	Lochsmidt number (2.7×10^{19} particles/cm^3)
O.D.	outside diameter
P	pressure
R	gas constant (1-atm/^{o}K-mole)
SEM	scanning electron microscope
SLM	standard liters per minute
S/N	signal-to-noise ratio
V_{BR}	breakdown voltage
epi	epitaxial
$h\nu_{1.27}$	energy of 1.27μ
$\bar{I}_{piston}$	average piston photocurrent
i_{piston}^{100}	photocurrent of piston source at 100 cm
$i_{piston}^{\bar{x}}$	photocurrent of piston source at $\bar{x}$
i_{std}^{100}	photocurrent of standard lamp at 100 cm
i_{Δ}	photocurrent from $O_2(^1\Delta)$
i.d.	inside diameter

k_{Δ}	rate constant for $O_2(^1\Delta)$
k_{NO-O}	rate constant for reaction of NO+O
ℓN_2	liquid nitrogen
n	moles
$\bar{x}$	average position of piston source in the measuring tube
$^1\Delta$	singlet delta, first excited electronic state of O_2
ΔP	pressure difference
$\delta\lambda$	spectrometer bandwidth (Angstroms)
τ	half-life of $O_2(^1\Delta)$ state

SECTION I
INTRODUCTION - PART ONE

1. BASIC PURPOSE

The basic objective of the research program reported here was to design, engineer, and build an effective generator of gaseous oxygen chemically excited to the $O_2(^1\Delta)$ state. This excitation of oxygen molecules to the first electronically excited state (about 0.9 eV above the ground state) was to be a direct result of the chemical reaction in the generator producing the oxygen. To be useful as a component in other Air Force Weapons Laboratory (AFWL) equipment it was necessary to define performance objectives for this generator in considerable detail.

2. DETAILED OBJECTIVES

The total oxygen generated was to be released through a tube 5 cm in diameter at a pressure of at least one torr and with a velocity of 2000 cm/sec. Of this total oxygen flow, at least 17% was to be excited to the $O_2(^1\Delta)$ state. Although chemically inert carrier gases such as nitrogen were permissible, water and other contaminating vapors were to be kept to strict minimums. The floor area available for the generator was a 4 by 4 foot square. A generator run should last at least 30 seconds, and runs should be repeatable indefinitely at periods separated by no more than 15 minutes. Lastly,

an implicit objective was the hope that the generator which evolved from this research would be scalable later to much larger output flows.

3. PROGRAM SCHEDULES

Part One of this research was scheduled for 9 months working time, which later was extended to 10. The first part of the program had essentially three phases of approximately equal length: (1) a preliminary phase during which an optimum chemical reaction was sought, (2) an intermediate phase of engineering and building a workable generator, and (3) a final phase of testing and reworking the generator to reach optimum operating conditions.

4. PROGRAM HISTORY

In practice, the plan outlined above worked quite well through the first two phases; both the time schedule and the objectives were met. In particular, following a series of preliminary experiments, the decision was made to generate $O_2(^1\Delta)$ from the chemical reaction of elemental bromine (Br_2) with a strongly alkaline solution of concentrated hydrogen peroxide (H_2O_2). The generator, constructed and operated during the second phase of the program, likewise proved to be a practical and versatile laboratory machine.

The third phase of Part One of the program was not completed as scheduled. Largely because of difficulties encountered in

measuring the rapidly flowing output gases, we could not continue as planned with a parametric study of all the operating conditions which should be adjusted to optimize the generator yield.

In particular, it was necessary to measure the concentration of $O_2(^1\Delta)$ in the output and also the total flow of unexcited O_2. Both of these measurements proved to be treacherously difficult to make with the necessary absolute accuracy. As a result, the time originally allocated for testing, reworking, and optimizing the generator had to be spent devising, building, and calibrating new instruments to measure $O_2(^1\Delta)$ concentration and total flow of O_2. Both of these instrument designs were concluded with some success. Thus, by the end of the first contract period, data gathered with these new instruments could be used briefly to assess the progress made up to that point in the laboratory generation of $O_2(^1\Delta)$.

5. SUMMARY OF RESULTS

Ongoing studies and experiments have tended to confirm that the relatively early decision to concentrate the research effort around the $Br_2+H_2O_2$ reaction was a very good choice among competing reactions. The generator, built to utilize this reaction, has been successful in many ways. It can run semi-continuously (45 minutes) rather than intermittently (30 seconds).

It is compact and straight-forward to build and operate. Many of the operating parameters can be varied to gain a better understanding of the physical-chemical mechanisms involved in the reaction. This versatility eventually may lead to an optimum output yield. In short, even in its present prototype form, the generator is a very useful piece of laboratory equipment.

The instrument which we had to devise for measuring the absolute concentration of $O_2(^1\Delta)$ is an apparently new optical configuration for the detection of low level luminosity in gaseous or liquid volumes. It uses a piston source as an intermediate absolute calibration reference. The method should result in accuracy improvements as great as 5 times and sensitivity improvements as great as 100 times over present methods used to measure weak light radiation from extended volumes. The scientific and practical importance of such an improvement will probably be widespread. For the application of primary concern here, it is now possible by optical fluorescence to monitor continuously the concentration of rapidly flowing $O_2(^1\Delta)$ to accuracies of a few percent. The apparatus used is rugged, reliable, and inexpensive.

Toward the direct objective of this research, the following progress is reported briefly here:

The better flows of oxygen generated a pressure of about 0.6 torr at a velocity of about 1000 cm/sec. This is within

a factor of three of the goal set in advance. This goal can likely be reached or exceeded simply by increasing the flow of reagents and if necessary the size of the apparatus. It is estimated that the maximum concentration of $O_2(^1\Delta)$ generated was between 8% and 15%, to be compared with a design goal of 17% $O_2(^1\Delta)/O_2$(total) or more.

The removal of water and other undesired end products was not conclusively explored. Vapors of Br_2 were still conspicuously present in the output flow after passing through cryogenic traps of conventional design. Results from some traps we designed especially for fast flows were incomplete but encouraging.

SECTION II

PRELIMINARY EXPERIMENTS

Initial experiments to produce $O_2(^1\Delta)$ chemiluminescence were made at atmospheric pressure. The first of these consisted of observing the reaction:

$$H_2O_2 + OCl^- \rightarrow H_2O + Cl^- + O_2\uparrow \qquad (1)$$

using 30% H_2O_2 and commercial NaOCl solutions. The reactants were mixed in a transparent cell by impinging two liquid jets. The visible chemiluminescence was faint and sensitive to the orientation of the jets.

In subsequent experiments, powdered $Ca(OCl)_2$ was used in place of the NaOCl solution and an increased dimol radiation was observed. The reaction by-products consisted of a large amount of insoluble salt suspended in water. In contrast to the NaOCl, the chemiluminescent reaction of $Ca(OCl)_2$ did not proceed when a small amount of water was mixed with the calcium salt, although unexcited oxygen was evolved.

A later series of benchtop experiments with hypohalite salts revealed a heretofore unreported observation. When NaOCl, NaOBr, or $Ca(OCl)_2$ were allowed to react with neutral H_2O_2, the typical red dimol emission was observed. However, when the H_2O_2 solution was made strongly acidic, the red chemiluminescence was enhanced considerably. Although the first experiments employed HCl

to acidify the peroxide, the reactions were repeated using HNO_3, H_2SO_4, H_3PO_4 and glacial CH_3COOH, and all gave similar results. It is known that for very dilute solutions the chemiluminescence peaks in the basic region (Ref. 1), but in concentrated acid solution the reaction mechanism apparently changes.

The use of various halogens with 30% peroxide was also examined in an early series of experiments. Initial tests were made with Cl_2 gas introduced into a beaker of peroxide solution through a porous glass frit. These tests gave no visible luminescence, although O_2 gas was formed. However, when the peroxide solution was made strongly basic ($\sim$ 12% NaOH by weight) the reaction produced bright chemiluminescence in a thin sheet just beyond the frit.

Another test consisted of using liquid Br_2 in place of Cl_2. The Br_2 was added by pipette to a basic peroxide solution. In this case the amount of visible radiation was most encouraging. When the Br_2 was introduced well below the surface of the peroxide solution, large O_2 bubbles were formed which appeared to be filled with the dimol radiation. This fluorescence persisted until the bubble broke the surface. Upon continued addition of large amounts of Br_2, the reaction persisted without noticable diminution until all of the Br_2 was used up, leaving behind a weakened but still clear peroxide solution. The stoichiometry of this reaction is described in Appendix A.

In order to minimize the time the excited oxygen is in contact with water, a procedure was conceived whereby the Br_2 would be frozen on the outside of a ℓN_2-filled cold finger, and the basic peroxide solution would then be sprayed onto the outside. This

experiment gave the same characteristic bright chemiluminescence as was observed for liquid Br_2.

In order to further investigate the obvious possibilities of the solid Br_2 reaction, an exploratory reactor was constructed. This is shown in Fig. 1. The cold finger consisted of a large test tube inserted through a lubricated hole in a 2 inch rubber stopper. The reactants were added by means of $\frac{1}{4}$ inch glass tubes on either side of the reactor, with Br_2 vapor being carried to one side of the cold finger and peroxide solution to the other. In these experiments the cold finger was turned manually while the Br_2 deposition rate was controlled by means of a throttle valve and a carrier gas (Ar). The peroxide was gravity-fed from a separatory funnel. A vacuum pump maintained the system at 1 to 5 torr.

The exploratory generator allowed several aspects of this method of generating singlet oxygen to be examined. The deposition of the Br_2 worked well: rotation of the cold finger produced an even band of frozen Br_2 where desired. The continuous regulation of Br_2 deposition was still a problem however, because under reduced pressure the Br_2 evaporated and froze in the reservoir, greatly decreasing the vapor pressure and hence the deposition rate. Upon being allowed to equilibrate with its vapor, the frozen bromine would then quickly liquify, increasing the subsequent deposition rate.

The peroxide reactant also presented a problem in that the solution tended to evaporate and freeze in the capillary tip under the reduced pressure of the system. Once the flow was initiated, however, the thermal mass of the peroxide prevented further freezing.

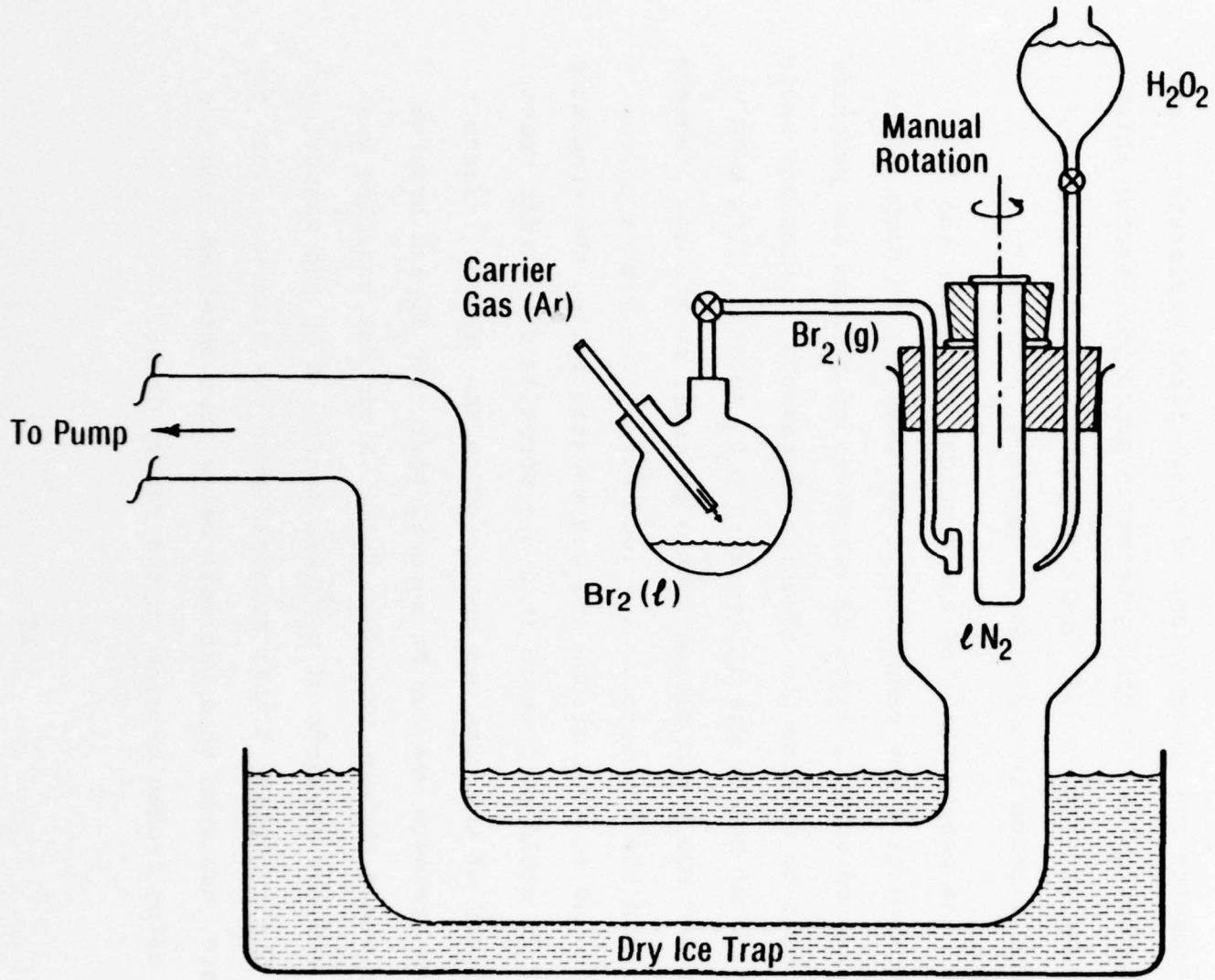


Figure 1. Preliminary Laboratory Equipment to Generate $O_2(^1\Delta)$

The reaction itself appeared to work quite well; a vigorous response was observed as the peroxide was sprayed onto the bromine. Use of excess H_2O_2 kept the cold-finger clean for subsequent redeposition of Br_2.

The results and observations of these first exploratory tests led to the design of the next generation prototype reactor which is described in Section III, and the operation of the generator with frozen bromine is examined in detail in Section V.

After the construction of the chemical generator and $O_2(^1\Delta)$ measuring apparatus was completed, it was possible to compare the efficiencies of various types of reactions of bromine and peroxide.

In order to examine the reaction of gaseous bromine and basic H_2O_2, a 250 ml beaker was filled with H_2O_2 solution (12% NaOH by weight in 30% H_2O_2) and placed upon a pedestal in the low pressure region within the generator. A $\frac{1}{4}$ inch Pyrex tube with a porous glass frit (40 to 60μ) at one end was mounted inside the generator such that it could be lowered into the peroxide containing beaker. The other end of the tube was connected to the bromine reservoir. The system pressure was set at several torr with N_2, and bromine vapor was added through the glass frit. A violent reaction was observed and the presence of $O_2(^1\Delta)$ was monitored by the measuring system. The strongest signal appeared when the frit was close to the surface, but even this was well below that obtained from the reaction using frozen bromine on the rotary dewar.

In another experiment, a 150 ml glass filtering funnel with a glass frit (10 to 15μ) was used as the reaction vessel. The funnel was supported inside the generator and filled with 30% peroxide solution. A tube connected the bottom of the funnel to a vacuum feedthrough, which in turn was connected to the bromine reservoir. The system pressure was set at several torr of N_2, and the bromine vapor was slowly introduced into the funnel. Again an $O_2(^1\Delta)$ emission was observed as the reaction proceeded. The depth of the H_2O_2 layer and the porosity of the glass frit were varied in several different experiments. The strongest signals were obtained when the gas bubbles had to traverse a minimum path length in water, but again these signals were well below those obtained in the frozen bromine experiments.

The presence of bromine in the generator output is undesirable for both the lifetime of the excited oxygen and for the purity of the desired end product. One possible way to eliminate bromine from the generator output is to eliminate it from the input by using NaOBr in place of elemental bromine.

No hypobromite salts are commercially available due to their instability at room temperatures (Ref. 2). However, it is possible to prepare fresh samples of some of the alkali metal and alkali earth salts and keep them for useful lengths of time at low temperatures ($\sim 0^{\circ}C$). The synthesis of NaOBr was therefore carried out following the procedure of Scholder and Krauss (Ref. 3). Rather than purifying the product, the NaOBr was left in solution (with some NaBr by-product) so that it could be introduced easily into the generator.

The experiment consisted of mounting two identical nozzles about 1" apart in the generator and aiming them so that both output streams intersected at the surface of the dewar (which was kept stationary and at room temperature). Acidic H_2O_2 (see above) and NaOBr solutions were loaded into the two nozzle reservoirs. The system pressure was set at several torr with nitrogen and both liquids were allowed to flow into the generator. The reaction was reminiscent of the early experiments using chlorine bleach and peroxide, with the interaction zone showing a vigorous, foamy reaction. No $O_2(^1\Delta)$ signal was obtained, however, during the course of the run. Upon later cleaning the downstream ℓN_2 traps, a large quantity of frozen bromine was discovered. It is postulated that the acid liberated the bromine from the hypobromite, although this was not seen in benchtop experiments at atmospheric pressure. A repetition of this experiment using neutral rather than acidic H_2O_2 and purified NaOBr was not carried out due to time limitations.

SECTION III

GENERATOR DESIGN AND FABRICATION

1. ASSEMBLY OF CHEMICAL GENERATOR

The chemical generator for $O_2(^1\Delta)$ developed in Part One consists of a glass reaction chamber fitted with a metal plate through which the reactants are fed, a dead-end gravity trap to contain the bulk of the by-products, and an output trap to remove the remaining impurities from the effluent gas stream. The generator incorporates features which offer maximum versatility in altering its configurations. All tube connections, for example, are made with O-ring or Teflon-lined fittings which can be quickly connected and disconnected, and connections to the reaction chamber itself are by adjustable O-ring feed-throughs. An overview of the system and the related measuring equipment is shown in Fig. 2 and a schematic diagram of the same is given in Fig. 3.

The reaction chamber, shown pictorially in Fig. 4 and schematically in Fig. 5, consists of a 10 inch section of 6 inch I.D. heavy-wall glass tubing from which there extends a 2 inch I.D. side arm. A stainless steel cylindrical band supplied the cold surface upon which the reaction takes place. It is centered in the chamber and is supported through a double O-ring rotating feed-through located in the top plate. The reaction band is rotated by means of a worm gear attached to the neck of the dewar which supports it and contains a refrigerating fluid. A specially designed solid state circuit keeps the driving speed

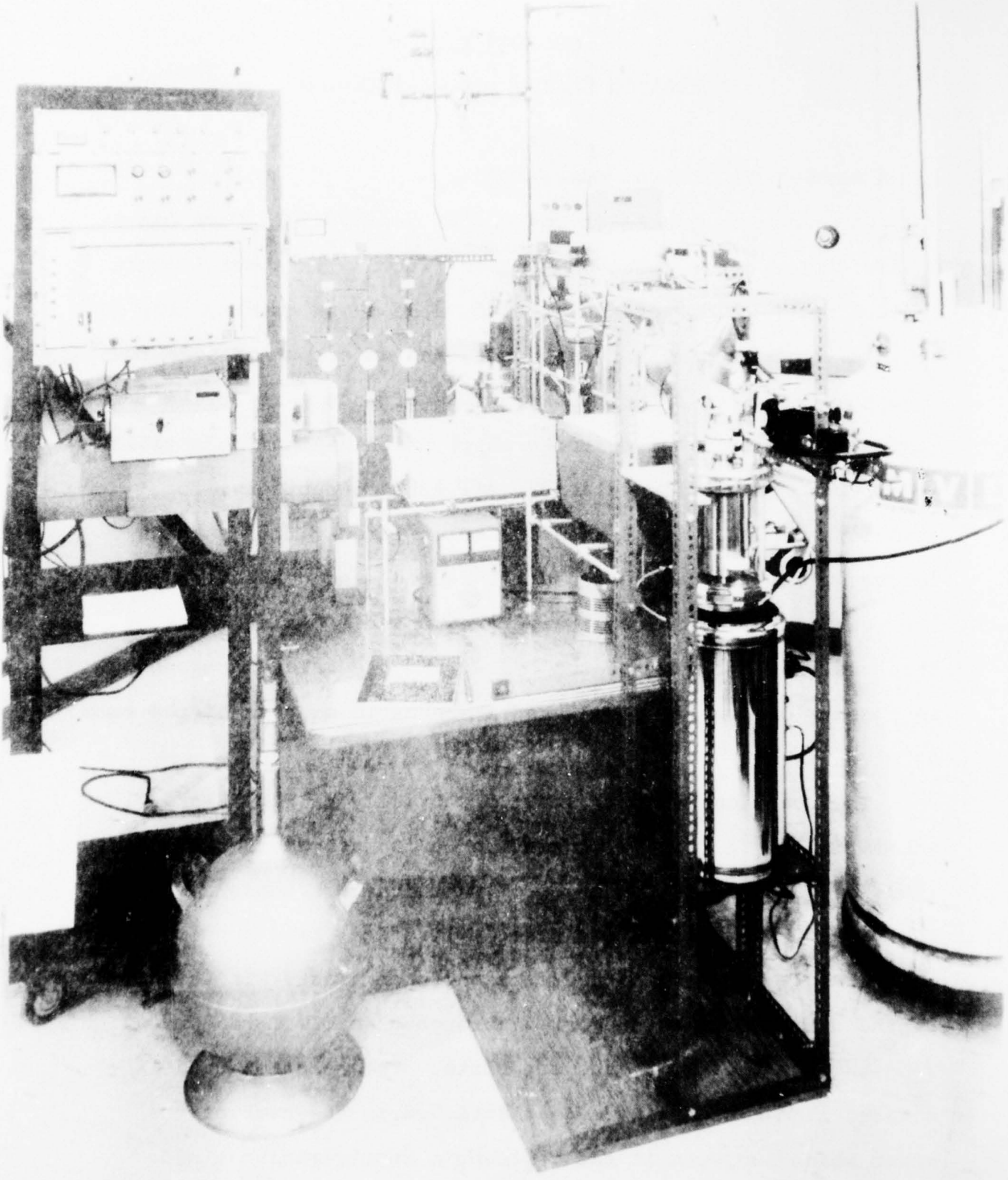


Figure 2. Photograph of Generator System

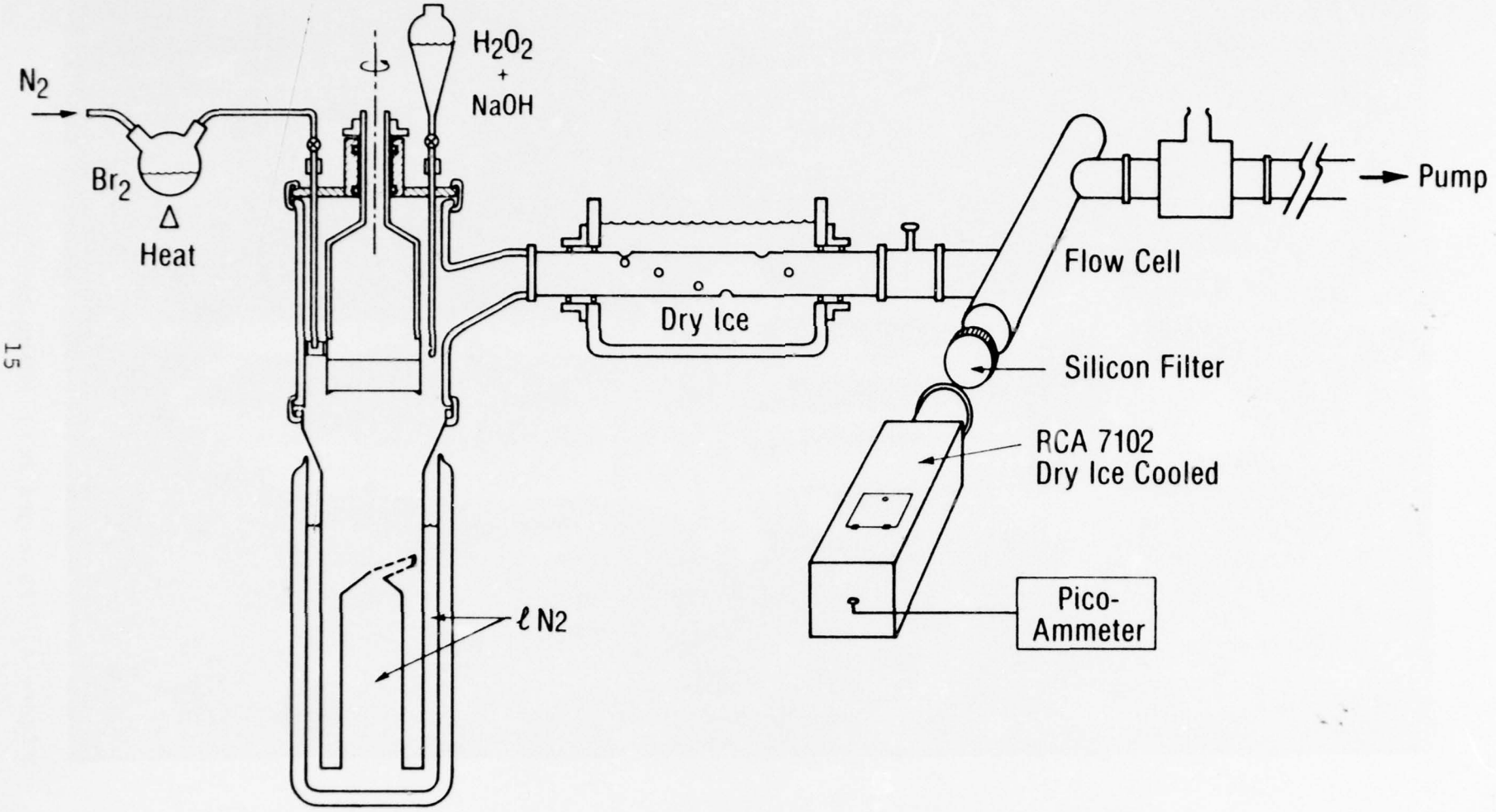


Figure 3. Schematic Diagram of Generator System

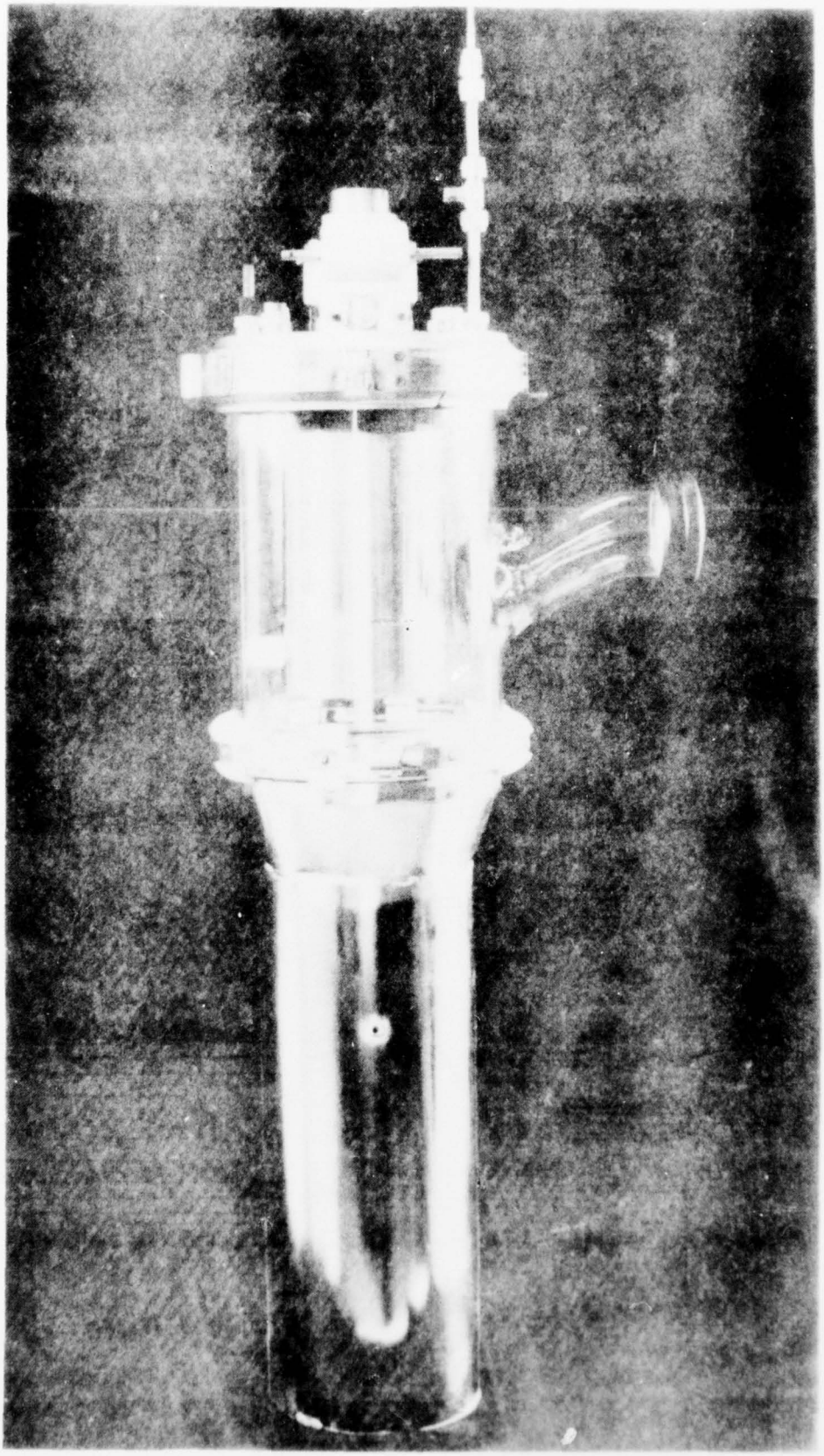


Figure 4. Photograph of Reaction Chamber

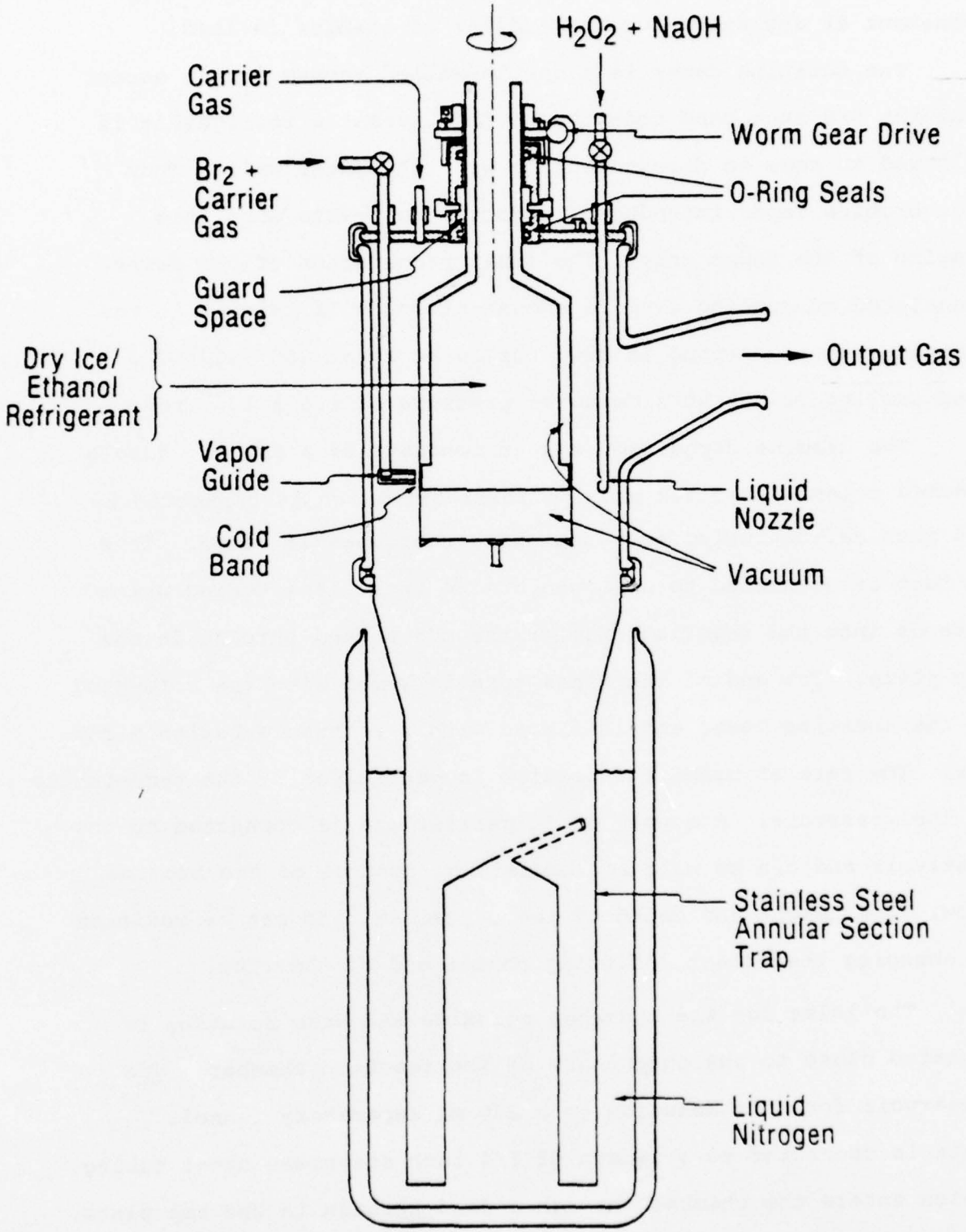


Figure 5. Schematic Diagram of Reaction Chamber.

constant at any set value, regardless of changes in load.

The rotating dewar is a double-walled vacuum bottle except for the 5/8 inch band near the bottom where the refrigerant is allowed to come in direct contact with the outer wall. Thus the bromine vapor introduced is forced to freeze onto this region of the dewar only. The final preparation of the dewar consisted of putting a small amount of molecular sieves in the vacuum region, pumping it down for 30 hours at 200°-320° C, and sealing it hot at a measured pressure of 1.6×10^{-6} torr.

The bromine deposition system consists of a 500 ml double necked erlenmeyer flask bromine reservoir which is connected by 1/4 inch Teflon tubing to a stainless steel needle valve. This in turn is connected to a length of 1/4 inch glass tubing which extends into the reaction chamber through a feed-through in the top plate. The end of the glass tube is level with the cold-band of the rotating dewar and is fitted with a removable Teflon director. The rate of bromine depostion is controlled by the temperature in the reservoir. A supply of N_2 carrier gas is connected to the reservoir and can be used for additional control of the bromine flow. The height and depth of the deposited band can be modified by changing the director fitting on the end of the tube.

The inlet for the hydrogen peroxide and base solution is located close to the output arm of the reaction chamber. The reservoir for this solution is a 250 ml separatory funnel. This is connected to a length of 1/4 inch stainless steel tubing which enters the chamber through a feed-through in the top plate.

A small hole in the tube (0.013 inch) directs a jet of peroxide solution onto the frozen bromine band, and a moveable device inside the stainless steel tube allows the hole to be cleared should clogging occur. Any frozen reaction by-products are removed from the cold-band of the dewar by a scraping blade located several inches past the reaction zone. Other inlets in the top plate are used to admit carrier gas, to mount pressure sensors, etc.

A stainless steel gravity trap refrigerated by liquid N_2 is located directly below the glass reaction chamber. It is a dead-end trap, designed to catch the bulk of the liquid and solid reaction by-products.

The output arm of the reactor is connected to a crucial second trap for the purpose of removing residual impurities from the effluent gas stream. The active length of that trap is 10 inches. It is crossed by nine 3/4 inch diameter tubes systematically arranged to increase the probability of gas contact with a cold wall. All surfaces within the trap are held at essentially the same low temperature by the surrounding liquid refrigerant. The trap is held by double O-rings on either end of an insulated box to shorten feed tubes and simplify cleaning.

The configuration described above constitutes the $O_2(^1\Delta)$ generator itself. For the purpose of measuring performance, an optical cell is connected to the output end of the generator. There is, in turn, an in-line ℓN_2 trap for back-up protection of the pumps.

Two vacuum pumps are available for use with this system. A local pump is used for small scale testing purposes. A much larger one (35,000 liters/min) for full scale runs is mounted on the building roof and is interconnected by a stainless steel pipe 6 inches in diameter.

2. SIGNIFICANT FEATURES

The most significant features of the design as described above are:

1) A cylindrical Pyrex low pressure reaction chamber 6 inches in diameter by about 6 inches high with 2 inch diameter outlet side tube.

2) On axis, a rotating motor-driven 4 inch diameter stainless dewar with a 5/8 inch high crcumferential cold strip near the bottom.

3) Gaseous feed for subliming bromine onto the cold band on the side away from the outlet.

4) Liquid feed of H_2O_2 onto the resulting solid bromine adjacent to the outlet.

5) A cold trap at the bottom of the reactor to freeze out excess reactants which are scraped from the rotating dewar.

6) Appropriate sources of inert carrier gas.

7) A carefully designed cold trap for stray bromine and water vapor in the outlet immediately beyond the reaction zone.

The resulting apparatus then has the following important operational properties:

1) All Pyrex surfaces with the exception of the stainless steel components which can be Teflon coated if necessary.

2) Short pathlenghts, wide apertures and minimum dead volumes.

3) Removal of excess water, reactants, and salts by gravity run-off into a secondary dead-end cold trap.

4) A carefully designed flow-through primary cold trap close to the reaction.

5) 100% concentration of halogen reactant in easily transportable solid form.

6) Generously long nearly steady state operating time.

7) Simple recharging and rapid clean out.

8) Ability to control the temperature at the reaction zone and in both cold traps independently.

SECTION IV

MEASURING EQUIPMENT

To carry this research effort to a full conclusion, the measurements required both explicitly and implicitly are the following:

1) Ratio of $O_2(^1\Delta)$ concentration to total O_2 concentration.
2) Delivery pressure of total O_2.
3) Partial pressure of water vapor.
4) Partial pressure of other contaminants including
   a) H_2O_2
   b) Br_2

Of these measurements, the first was of primary concern and its execution by the prescribed optical fluorescence method implied an accurate solution to the second measurement as well. These measurements proved to be so difficult, treacherous, and time consuming that they became the limiting factor in the progress of the generator development effort. These problems finally yielded to experimentally satisfactory solutions which are described in detail in this section. No time remained to attempt to meet the third and fourth requirements, although presumably these measurements would be much easier because only upper limit accuracy is needed.

The method prescribed for the measuring of excited oxygen concentration, $[O_2(^1\Delta)]$, was by absolute photometry based on its spontaneous radiation at a wavelength of 1.27_{μ} in the near infrared.

The desired accuracy of a few percent represents the practical limits of absolute photometry under the best experimental conditions. In this case, the conditions are far from ideal because the source is weak and extended in volume and because detectors for radiation at the prescribed wavelength are relatively insensitive and unstable.

The problem was solved by inventing a new photometric configuration, called the piston source, which can make measurements which combine the necessary accuracy and sensitivity. The accuracy is confirmed by an experimental comparision with published values of the chemiluminescence produced by the reaction NO+O.

To make effective use of the foregoing measurement, it was also necessary to measure the concentration of total oxygen, $[O_2]$, generated. Following this, it is trivial to calculate the required ratio of concentrations. Apparatus was designed, built, and calibrated to measure the $[O_2]$ in a small continuously flowing sample of the total generator discharge. The method was the chemical reaction with hot copper to remove oxygen from one of two otherwise identical arms of the pneumatic equivalent of an electrical wheatstone bridge. The measured pressure difference can then be related to $[O_2]$ when appropriate pressures and flows are known, by readings of conventional instruments. The method is fully described later in this section.

1. DETECTION OF SINGLET DELTA MOLECULAR OXYGEN

a. Photomultiplier Detection

The presence of $O_2(^1\Delta)$ can be detected and relative measurements can be made using the optical system depicted in Fig. 6 . The detection system is designed to be sensitive to the 1.27μ emission from the $^1\Delta \rightarrow {}^3\Sigma$ transition. The range of sensitivity extends from the cut-off of the S-1 photo-surface at 1.4μ to the cut-off of the silicon filter at 0.95μ. Peak sensitivity occurs at 1.05μ and the sensitivity at 1.27μ is 2.5% of that at the peak (see Figure 8). The RCA photomultiplier is maintained at dry ice temperature, and under these conditions, $O_2(^1\Delta)$ emission signals are obtained two orders of magnitude higher than the tube dark current and three orders of magnitude above the noise level. The photomulitiplier views end-on a cylindrical glass tube which is silvered on the outside to increase photon collection.

b. Spectroscopic Analysis

The optical system depicted in Fig. 7 is used to provide a spectral analysis of the emission from the $O_2(^1\Delta)$ flowing through the cylindrical flow tube. It is used also in quantitative studies of the $O_2(^1\Delta)$ emission. The spectrometer is a 0.8 meter, f/10.5, Ebert-Fastie monochromator, using a 600 line/mm grating blazed for 1μ. Curved slits 5mm wide and 25mm high provide a resolution of 155Å. High resolution is not important in the present work, and wide slits are used to provide measureable signals. The spectral response of the spectrometer-detector system , as

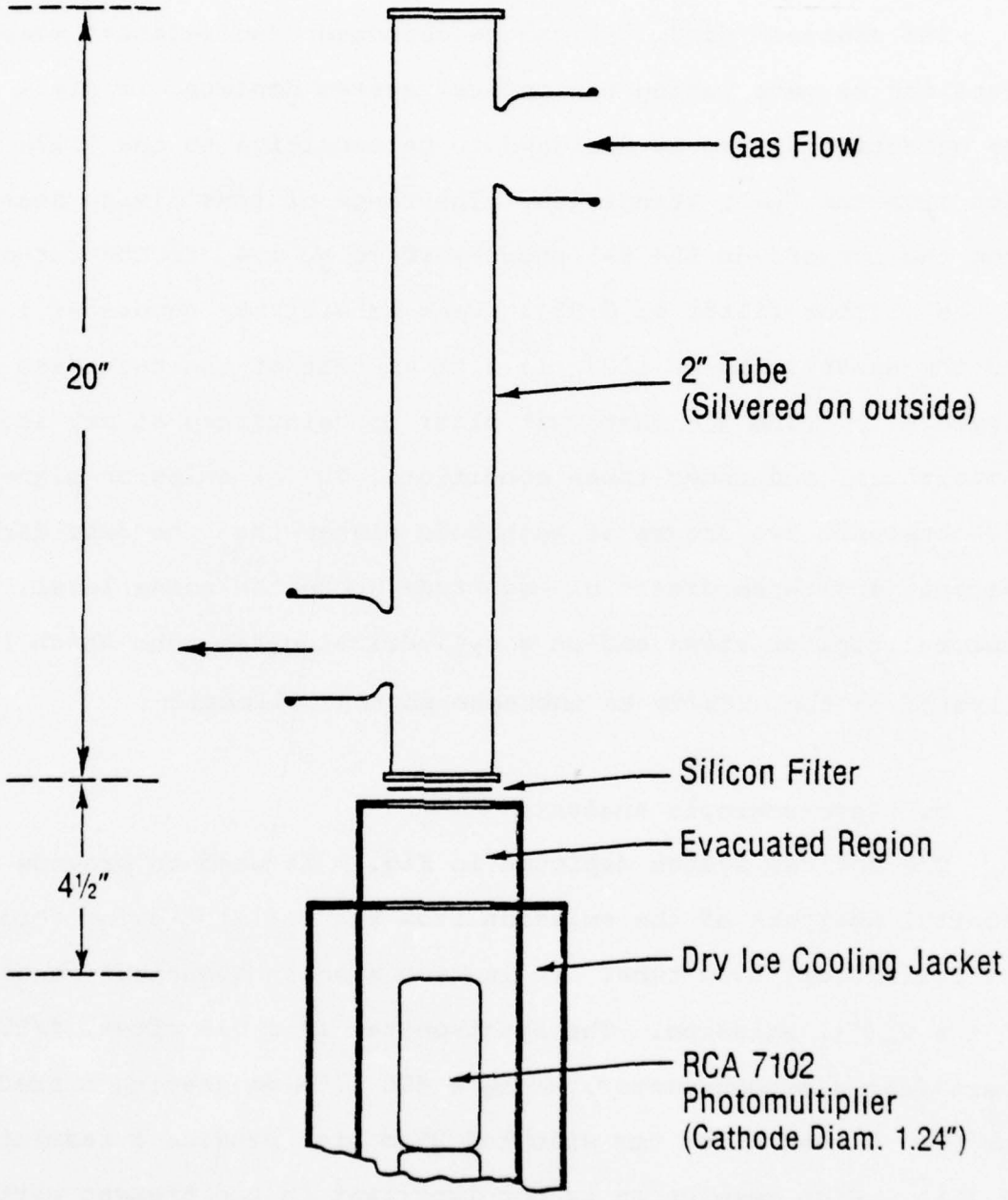


Figure 6. Optical Detection System for $O_2(^1\Delta)$

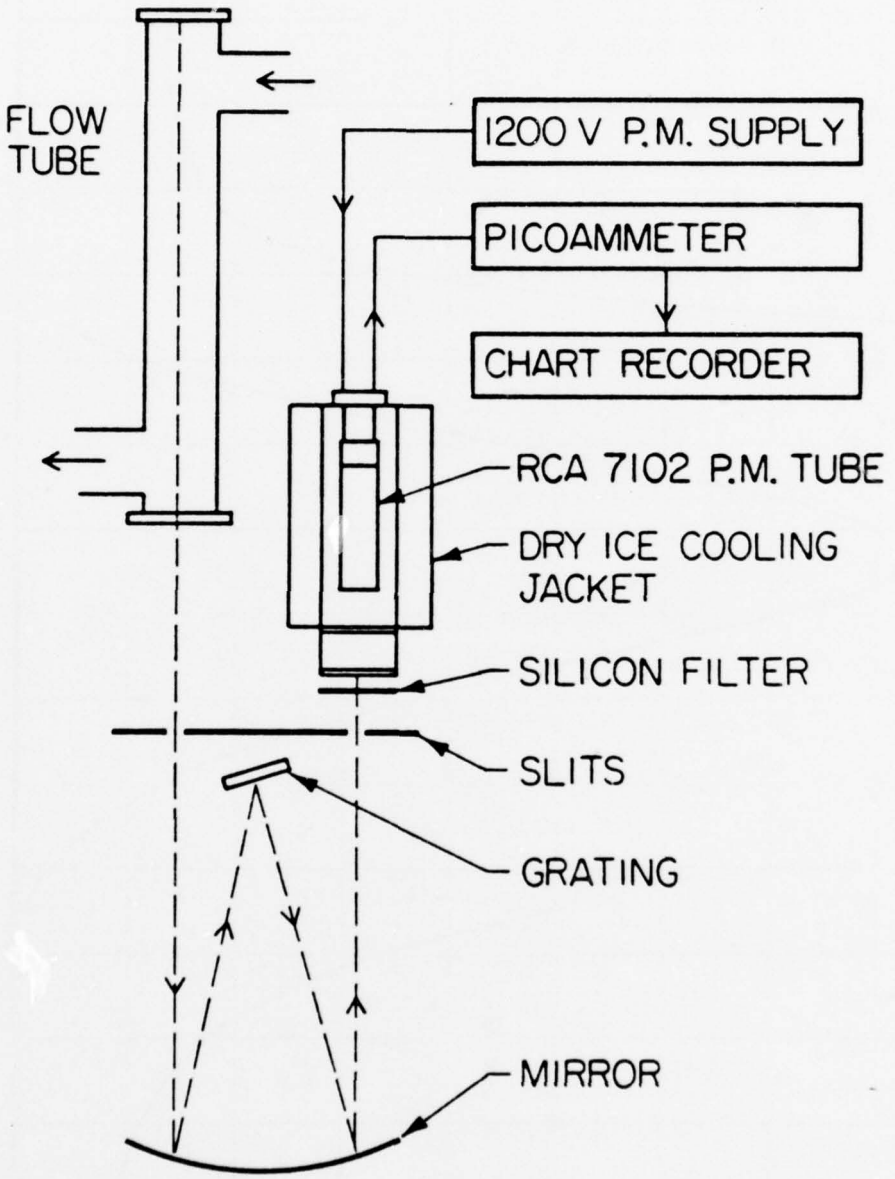


Figure 7. Optical System for Spectroscopic Analysis

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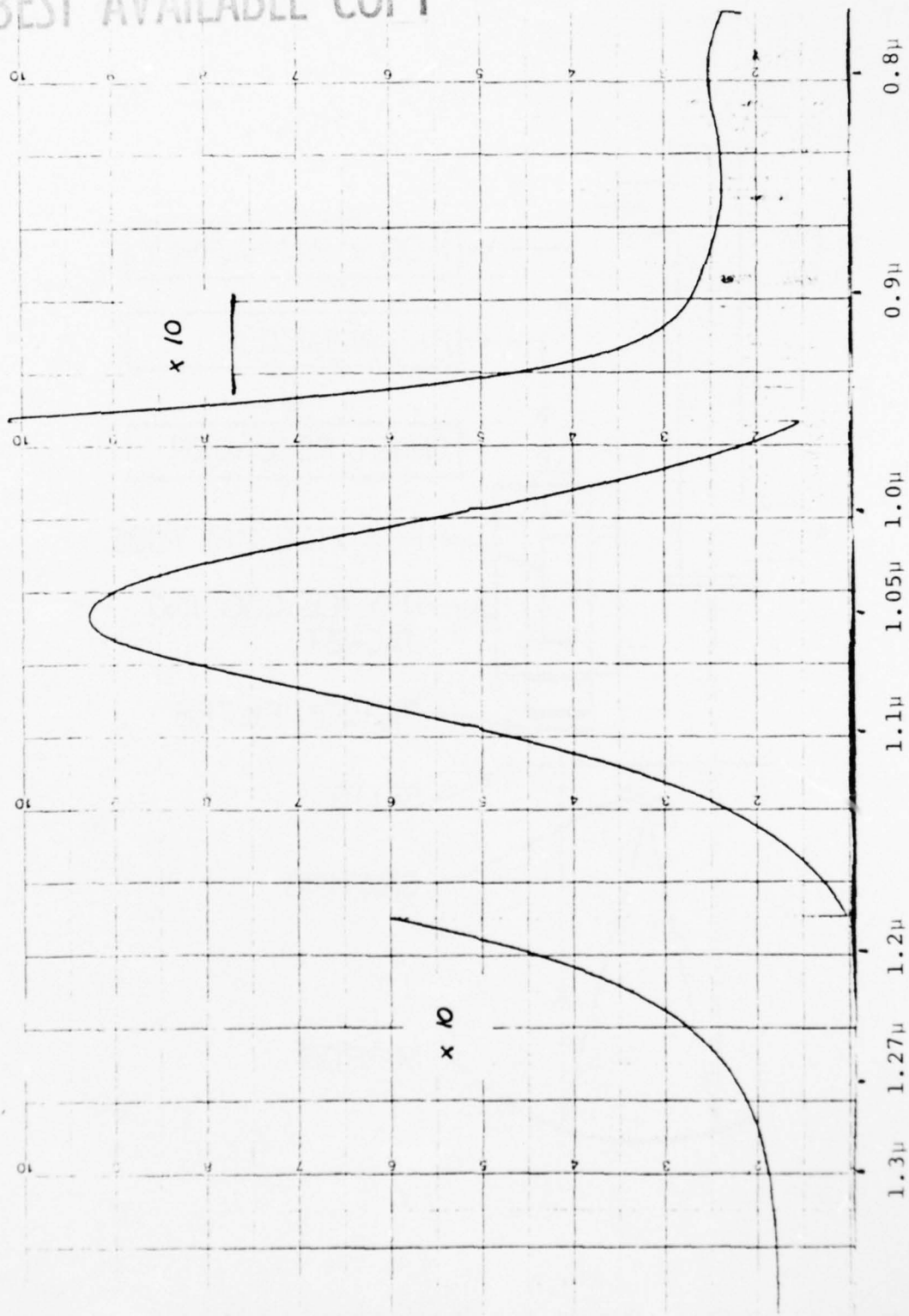


Figure 8. Detector Response

shown in Fig. 8 , was determined using a tungsten filament lamp of relatively uniform output over the wavelength range of interest. The peak at 1.05μ represents a crossover point of the individual response curves of the silicon filter and photomultiplier.

A typical spectral scan of fluorescence from $O_2(^1\Delta)$ produced by the chemical generator is shown in Fig. 9 . It is evident that the signal-to-noise ratio remains adequate for spectroscopic analysis. There is no evidence of any radiation over the range of the detection system other than that of $^1\Delta \rightarrow {}^3\Sigma$ at 1.27μ. The optical system described above therefore measures only $^1\Delta \rightarrow {}^3\Sigma$ radiation in this practical application.

c. The NO-O System

The first measurements of $O_2(^1\Delta)$ concentration were made by comparing the $O_2(^1\Delta)$ fluorescence with the chemiluminescence produced by the $NO + O \rightarrow NO_2 + h\nu$ reaction. The optical system of Fig. 7 is used in this comparison study. The inlet arm of the cylindrical flow tube is connected in turn to the $O_2(^1\Delta)$ chemical generator and the NO-O reaction system. The latter is depicted in Fig. 10. Oxygen atoms are produced by flowing oxygen (Linde Extra-dry, 99.6%) through a 1/2 inch O.D. quartz tube enclosed in a microwave cavity. These react with NO (Linde, 98.5%) which flows into the reaction zone from the opposite direction through a second inlet. Both flows are then mixed at a right angle bend followed by expansion in a 1 inch diameter to 2 inch diameter constriction, and finally by cross flow into the 2 inch diameter cylindrical measuring tube. The O_2 and NO flows are regulated by needle valves

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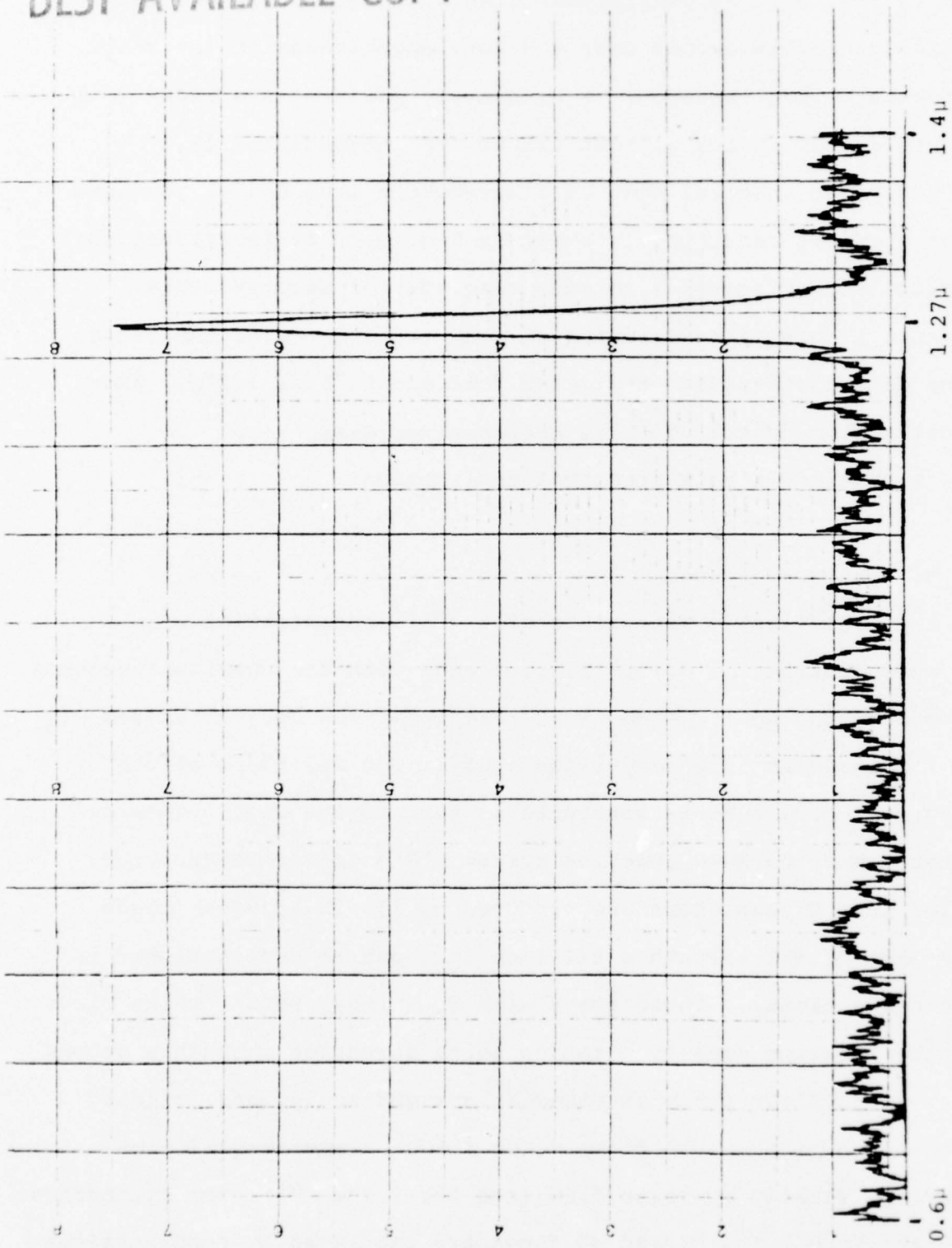


Figure 9. Recorded Spectrum of $O_2(^1\Delta)$

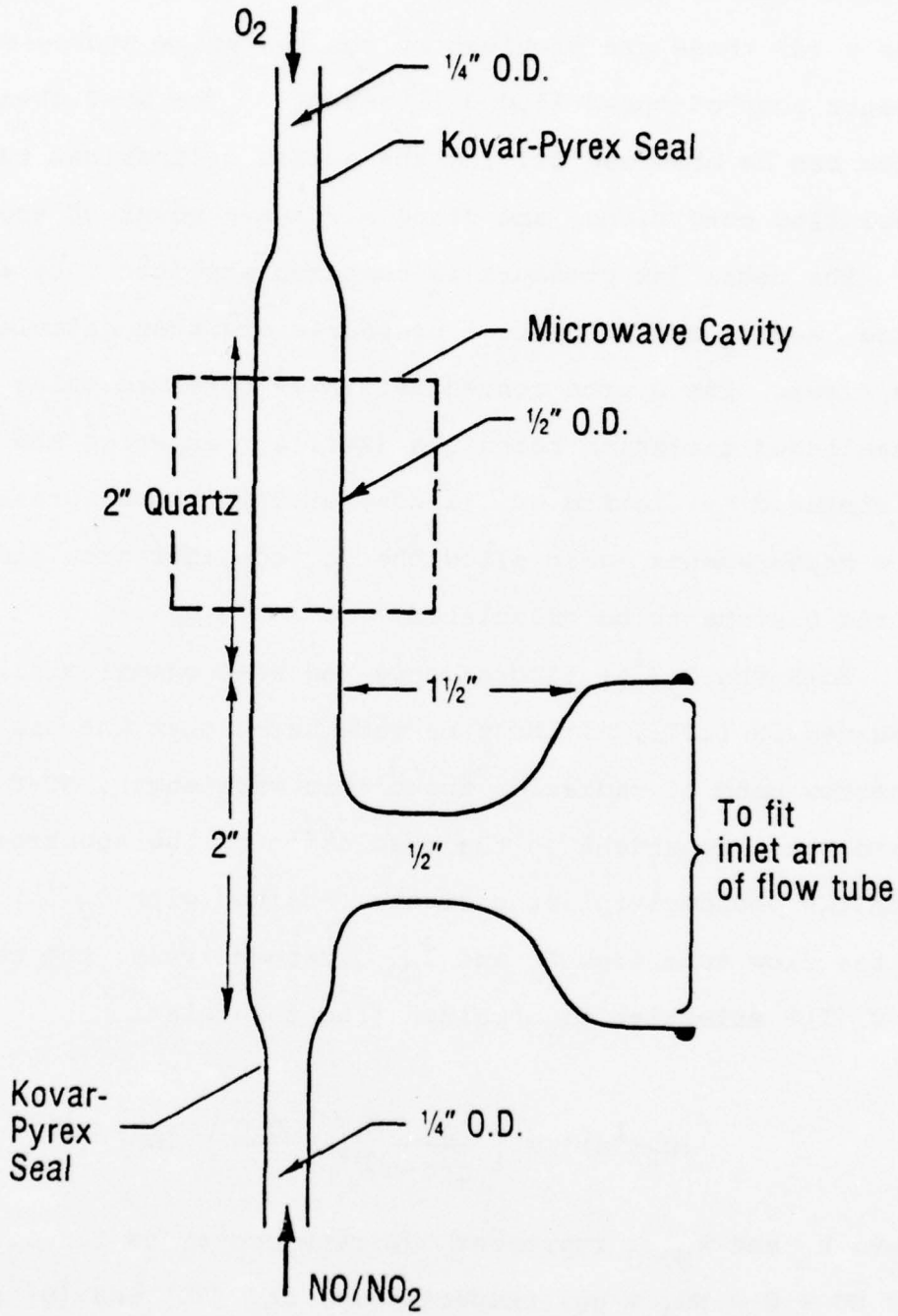


Figure 10. NO-O Reaction System

and measured by Linde flowmeters. Flows of up to 0.5 SLM have been used; these are provided by the two-stage Stokes mechanical booster pump of speed 35,000 litres/min. The NO-O chemiluminescence can be observed filling the entire cylindrical tube under these flow conditions and using microwave power of around 100 W.

The total gas pressure is measured absolutely by a McLeod gauge and O_2 and NO partial pressures are then calculated from the flows. The O atom concentration is obtained using the well-established titration technique (Ref. 4) in which the flowing NO is replaced by flowing NO_2 (Linde, 99.5%). Total pressure and flow measurements again allow the NO_2 concentration and hence that of the O atoms to be calculated.

Both the $O_2(^1\Delta)$ fluorescence and NO-O chemiluminescence are observed in 1.27μ. It must be remembered that whereas $O_2(^1\Delta)$ emits a narrow band of radiation about this wavelength, NO-O provides a broad band, dependent on the resolution of the spectrometer. From the photomultiplier currents obtained with $O_2(^1\Delta)$ and NO + O in the flow tube, i.e. I_Δ and I_{NO-O}, respectively, the concentration of $O_2(^1\Delta)$ molecules is obtained from the relation

$$[O_2(^1\Delta)] = \left(\frac{I_\Delta}{I_{NO-O}}\right)\left(\frac{k_{NO-O}}{k_\Delta}\right) [NO]\ [O] \qquad (2)$$

where k_Δ and k_{NO-O} represent the rate constants for $O_2(^1\Delta) \rightarrow {}^3\Sigma(O_2)$, and $NO + O \rightarrow NO_2 + h\nu$, respectively, and [NO] and [O] represent concentrations. k_Δ is taken as 3.7×10^{-4} sec^{-1}, assuming a 45 minute halflife (Ref. 5) for $O_2(^1\Delta)$. k_{NO-O} was calculated as follows. Golde et al. (Ref. 6) give a value for k_{NO-O} at 1.51μ

of $2.4 \pm 0.8 \times 10^{-17}$ cm^3 sec^{-1} μm^{-1}. (Ref. 7) Their curve on NO-O chemiluminescence as a function of wavelenght shows $I_{1.27}/I_{1.51} \simeq 2$, so that k_{NO-O} at 1.27μ may be taken as $4.8 \pm 1.6 \times 10^{-19}$ cm^3 sec^{-1} μm^{-1}. For the 155 Å band (resolution of spectrometer), this becomes

$$k_{NO-O} = 7.4 \pm 1.6 \times 10^{19} \text{ cm}^3 \text{ sec}^{-1} \qquad (3)$$

Such an analysis of the $O_2(^1\Delta)$ produced by our chemical generator has provided a value for the $O_2(^1\Delta)$ concentration of 3×10^{15} cm^{-3}, i.e., a pressure of 0.08 torr. The error in this value is difficult to assess. The stated error in k_{NO-O} of 30% may be pessimistic. The calculation of $[O_2(^1\Delta)]$ assumes that both the NO-O chemiluminescence and $O_2(^1\Delta)$ fluorescence fill the cylindrical flow tube uniformly. The errors in [NO] and [O] are estimated to be less than 5%.

d. The Piston Source

The NO-O calibration technique is inconvenient to use and contains errors which are difficult to eliminate. On the other hand, conventional techniques using a standard lamp source in conjunction with computation to allow for the geometry of the experimental system are also inconvenient and error-prone. This inconvenience and inaccuracy is largely eliminated by using a new calibration technique which was developed as part of the present study. (Ref. 8) The new technique uses a piston source whose construction is shown in Fig. 11.

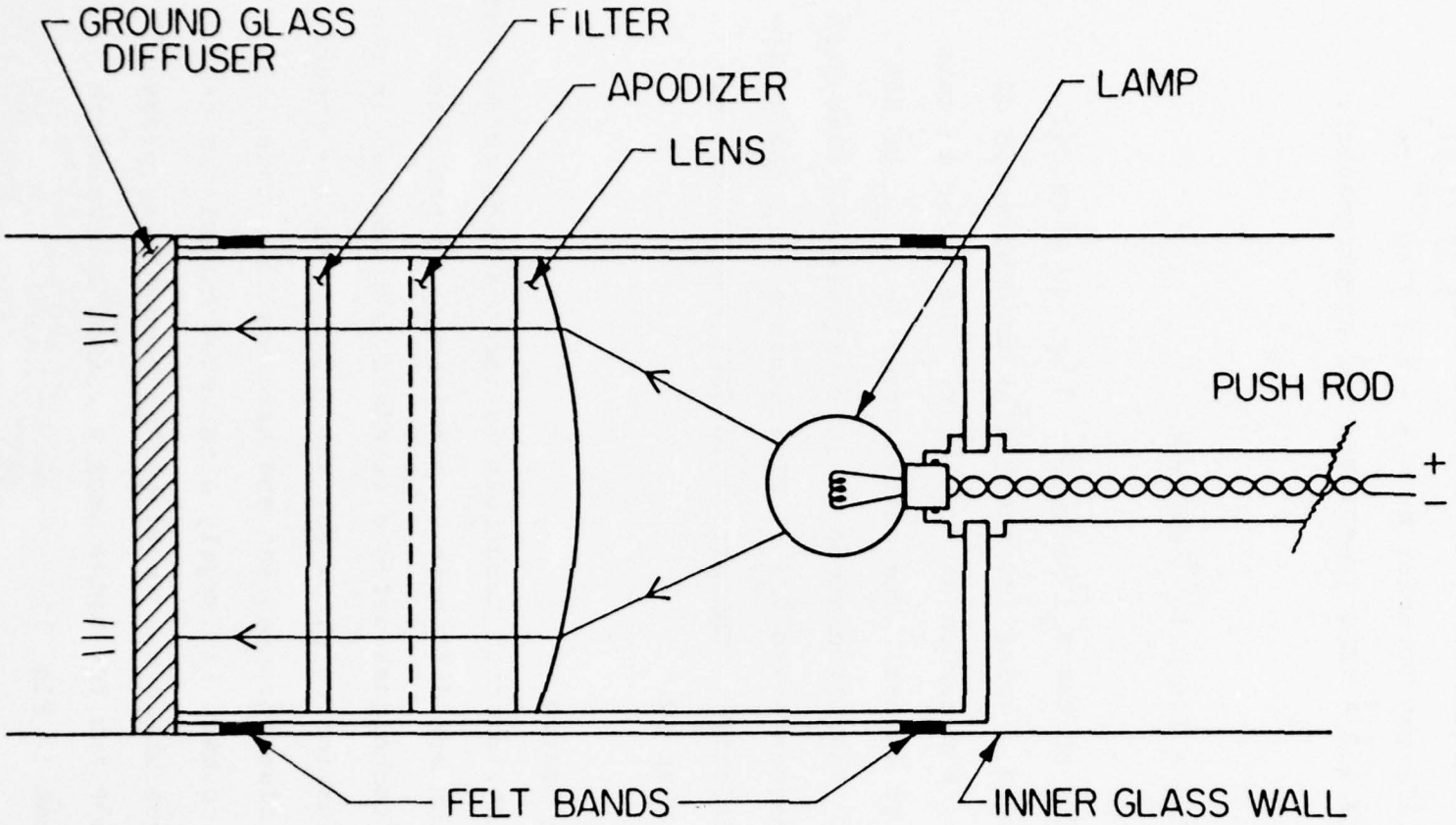


Figure 11. Sliding Piston Calibrated Source

A small tungsten filament bulb powered by a constant current supply (0.9A) is placed at the focus of a short-focus lens. The resultant parallel light passes through a diffuser and a combined negative fly's eye/diffuser. Ideally, the resultant light emitted by the piston source should be uniform across its surface and be uniform also over the emission angles to be used in the measurement. The components of the piston source are employed as shown in an attempt to provide this uniformity, and deviations from the ideal will be discussed. Optional provision is also shown for the utilization of a dielectric interference filter under nearly ideal operating conditions. The piston source is a close sliding fit to the inside of the cylindrical flow tube (see Fig. 6 and Fig. 7).

When the piston source is placed at any position along the length of the tube, its light-emitting face can be taken to represent an infinitely thin layer of fluorescent gas at that same position. By sliding the piston source along the tube, every layer of the volume of gas filling the tube can be simulated in turn by the piston source at the corresponding position; provided, therefore, that the piston source appears at the detector to be as uniform as the corresponding fluorescent gas layer, a comparison can be made of the light from the whole gas volume with the light from the piston source. If the absolute light output of the piston source is known, an absolute measurement of the fluorescence from the gas can be made.

The detection system used in the piston source experiments is that of Fig. 7 , with the spectrometer slit placed 60 cm from

the end of the flow tube, whose diameter is 5 cm. This means that the aperture of the spectrometer (f/10.5) is being efficiently utilized. It means also that only light from the piston source being emitted over angles of $\tan^{-1}\left\{\frac{2.5}{60}\right\}$ is being collected by the spectrometer. Uniformity of emission with angle is therefore not a problem in this arrangement, since for the cosine distribution of light from the diffuser, negligible variation of emission occurs over such small angles, i.e., the piston source appears similar to a layer of fluorescent gas emitting spherically. We have found through a series of experiments that quite large variations in light output over the surface of the piston source also are not important. The details of using and calibrating the piston source are discussed in Appendix II. As is shown there, the result is a partial pressure of $O_2(^1\Delta)$ equal simply to the photomultiplier current times a known calibration constant. The repeatability of these measurements is about 2%, and the absolute accuracy is about 5%.

e. Microwave Discharge Generation of $O_2(^1\Delta)$

The NO-O reaction system depicted in Fig. 10 readily lends itself to the microwave discharge generation of $O_2(^1\Delta)$, simply by shutting off the NO flow. The $O_2(^1\Delta)$ fluorescence from this system was investigated to provide a comparison with the chemical generator and to check the possibility that it might be used in the future as a secondary calibration standard in chemical generator output measurements.

Oxygen flows were in the range 0.008 to 0.25 SLM; the micro-

wave power was maintained at 100 W, and all cavity adjustments were made to optimize the signal at 1.27μ due to $O_2(^1\Delta)$ fluorescence, as measured using the system of Fig. 7 . There is always faintly visible NO-O chemiluminescence filling the flow tube under these conditions, but the NO-O signal is negligible at 1.27μ compared to the $O_2(^1\Delta)$ signal. The pressure of O_2 in the system was varied over the range 0.19 to 4.2 torr by varying the flow. It was found that $O_2(^1\Delta)$ signal was a function only of pressure over the range of flows employed.

The results of the measurements are displayed in Fig. 12 and Fig. 13 . The flat top to the curve of fluorescence vs pressure (Fig. 12) suggests that this system might have a use as a secondary standard for the measurement of $O_2(^1\Delta)$ and also as a stable general laboratory source since control of the oxygen pressure over a range of almost 2 torr is not cirtical.

Fig. 13 shows that the efficiency of $O_2(^1\Delta)$ production using microwaves is optimized at an input O_2 pressure around 0.3 torr. Under these conditions, the output concentration of $O_2(^1\Delta)$ as measured by the piston source was 8%. This measurement is probably pessimistic, however, because it dropped rapidly with distance from the source,suggesting that the $O_2(^1\Delta)$ generated by the microwaves was being quenched within the measuring tube itself. Thus steps would have to be taken to remove quenchers promptly from the flow before such a source of $O_2(^1\Delta)$ could be a reliable laboratory tool. We did not try to do this within the scope of this work.

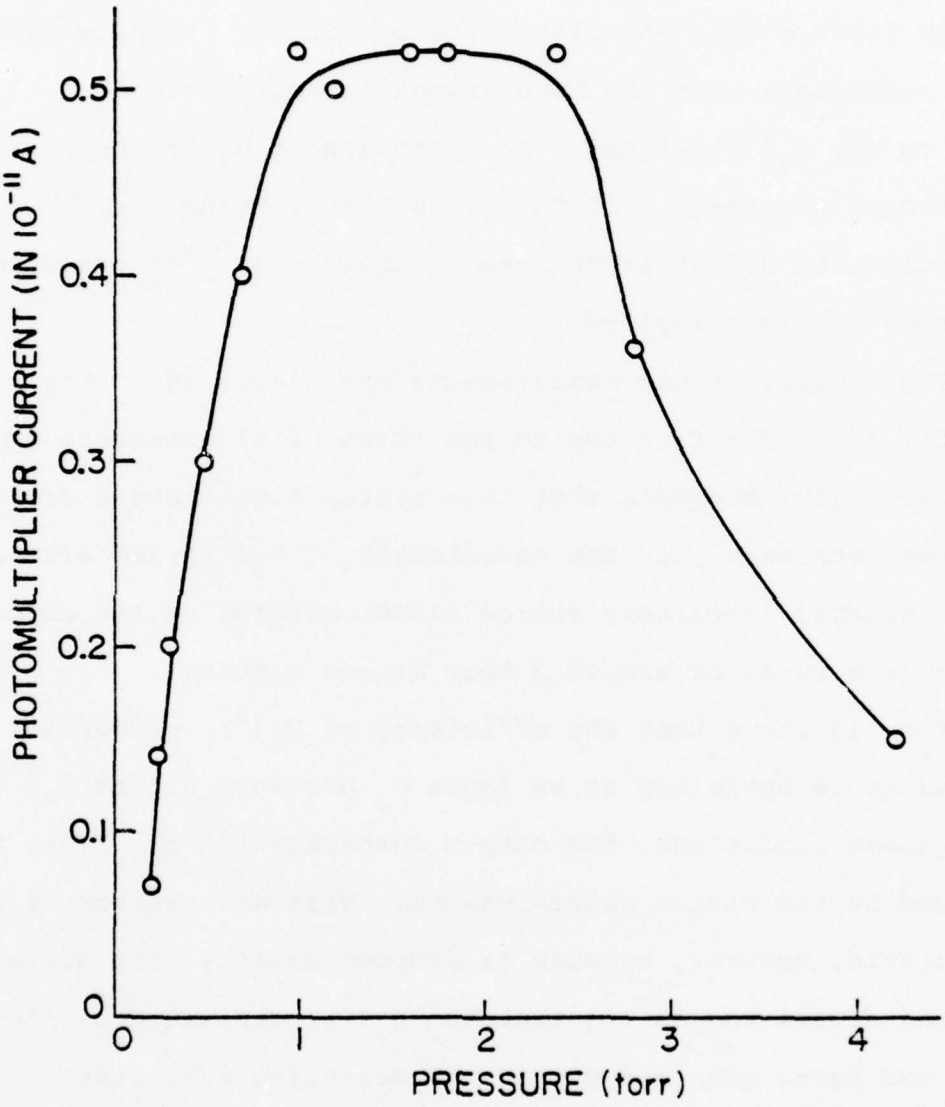


Figure 12. $O_2(^1\Delta)$ Fluorescence vs. Pressure

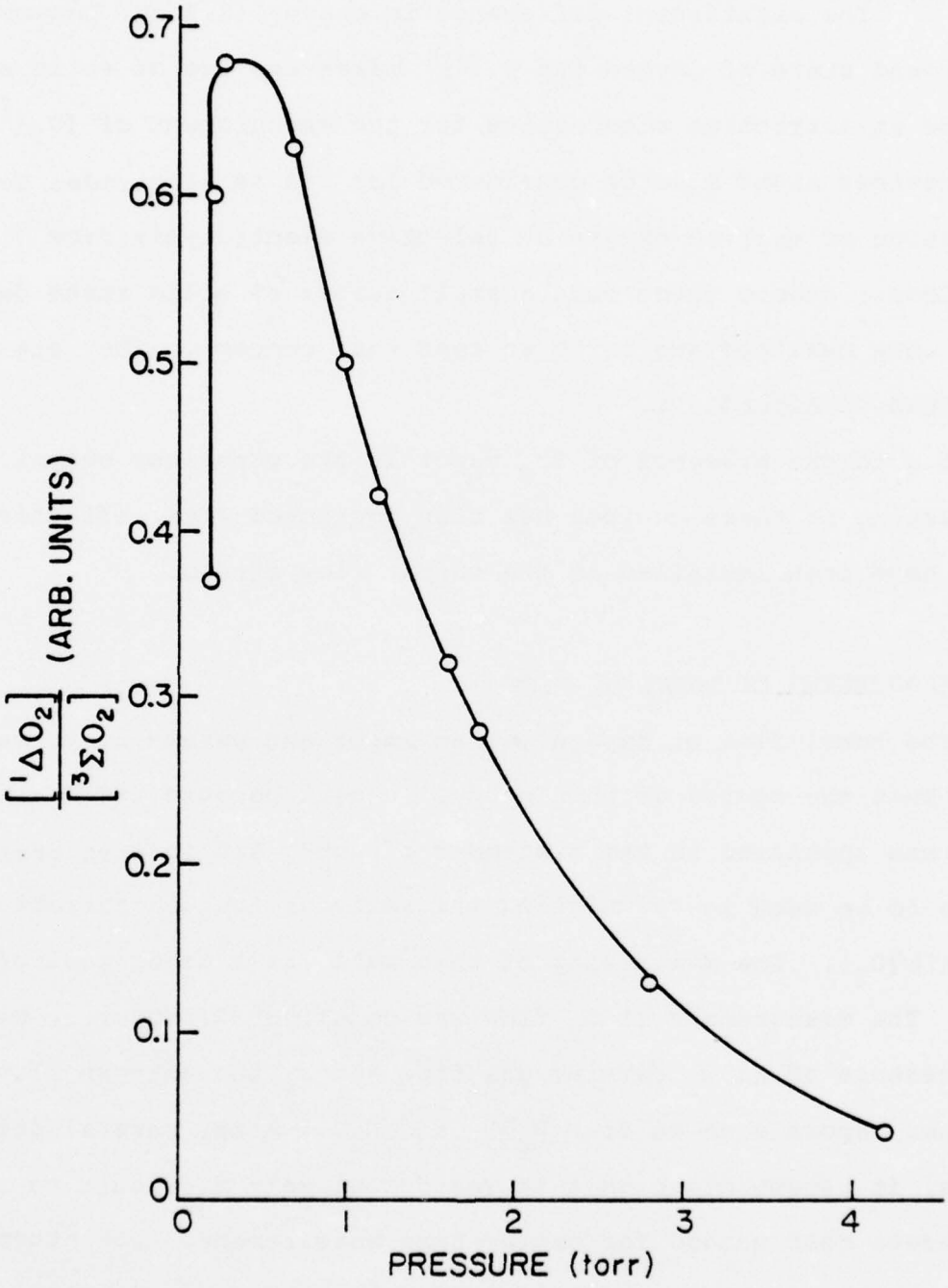


Figure 13. $[O_2(^1\Delta)]/[O_2(^3\Sigma)]$ vs. Pressure

f. Solid State Methods

The significant difference in energy (0.9 eV) between the ground state of oxygen and $O_2(^1\Delta)$ makes the use of solid state devices an attractive alternative for the measurement of $[O_2(^1\Delta)]$. Such devices might also be considered for use as electrodes for the generation of excited oxygen by selective electrolysis from solutions. Toward these ends a small number of solid state devices were designed and built to test that concept. They are described in Appendix C.

Due to the presence of Br_2 vapor in the generator output, the testing of these devices has been postponed until effective traps have been installed in the output flow stream.

2. MEASUREMENT OF TOTAL O_2 FLOW

The total flow of oxygen was an important parameter to measure throughout the course of this study, in part because its minimum value was specified in the statement of work, and in part because it was to be used in calculating the ratio of the concentrations, $[O_2(^1\Delta)]/[O_2]$. The maximizing of that ratio is a major goal of this work. The measurement of O_2 flow was complicated, however, by the presence of an N_2 carrier gas flow and by the unknown flows of other vapors such as Br_2, H_2O_2, and H_2O. After several false starts, it became clear that it was deceptively difficult to find a moderate cost method for making this measurement. One attempt to solve this problem was to design a new kind of measuring system which was built and tested, but unforturnately very late in the program schedule.

The new scheme devised for measuring the total flow of oxygen from the $O_2(^1\Delta)$ generator is shown diagrammatically in Fig. 14. The measurement is based on a known flow through the whole system of a chemically inert, low boiling point carrier gas, such as nitrogen. A few percent sample of the total flow, extracted continuously from the output flow, is passed through a specially designed cryogenic trap to remove all Br_2, H_2O_2, and H_2O vapors. It then passes through a double-path tubing system which is the pneumatic equivalent of an electrical bridge. The equivalent pneumatic bridge generator now consists of a small auxilliary roughing pump, and the detector is a differential pressure gauge. At the detector corners of the bridge are rigid chambers, identical except that one contains a large surface area of heated copper to remove oxygen chemically, whereas the opposite chamber passes oxygen freely. The resulting difference in pressure under flowing conditions is used as a measure of the fraction of total oxygen present based on a calibration using known artifically produced flows of oxygen and nitrogen as a reference.

In reduction to practice, the rigid chambers have stainless steel walls. The pneumatic resistance bridge is assembled from four identical adjustable metering valves which can be set for a practical response time, balanced using pure nitrogen flow, and then locked for calibration and use. An appropriate temperature for the copper-oxygen reaction was found to be 325°C. The copper (in the form of lathe turnings) can be replaced if ever necessary. In normal operation, the accumulated hot copper oxide is reduced by hydrogen without removel from the sealed chamber. Fig.15 is a

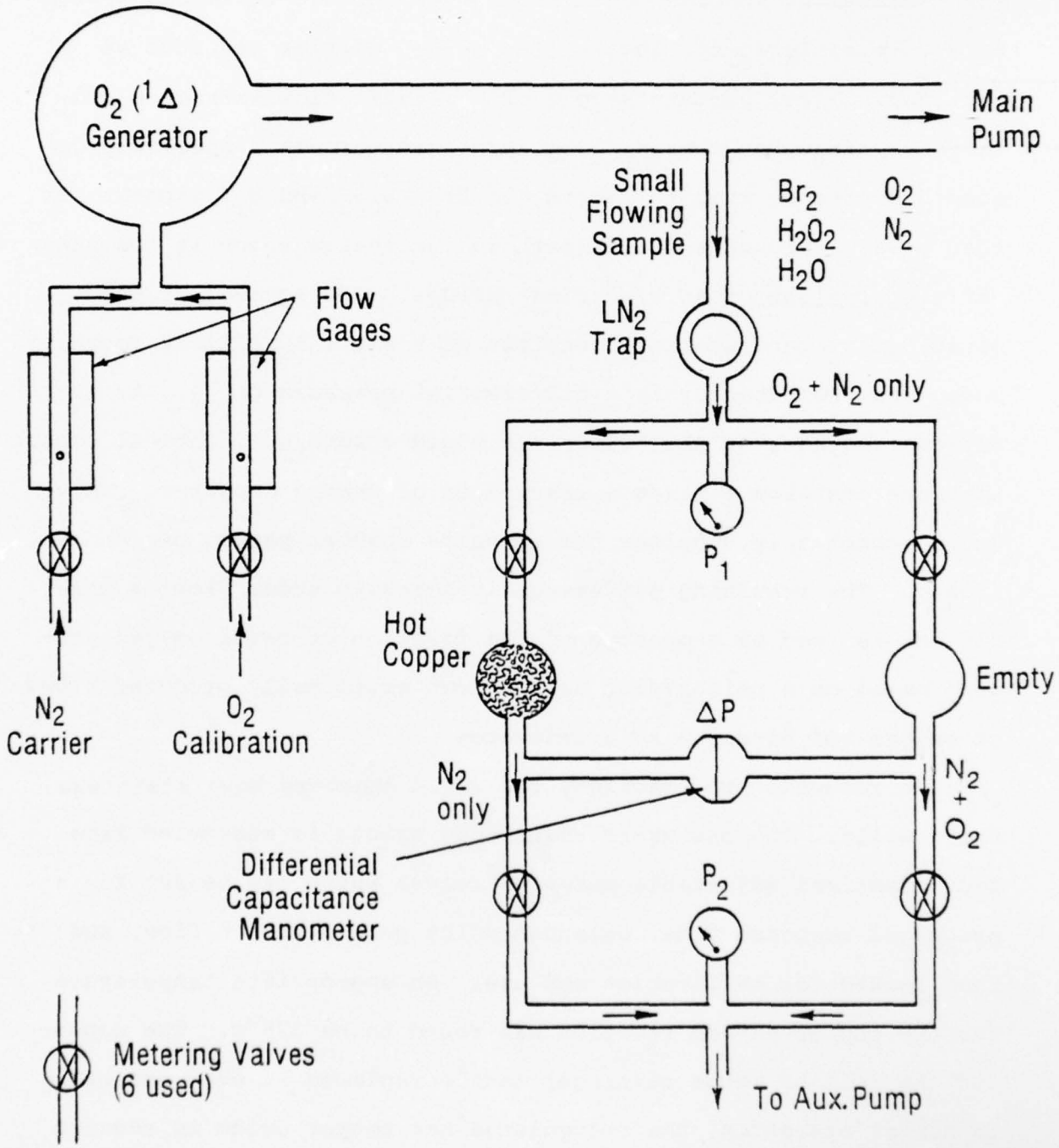


Figure 14. Measurement of Flowing O_2

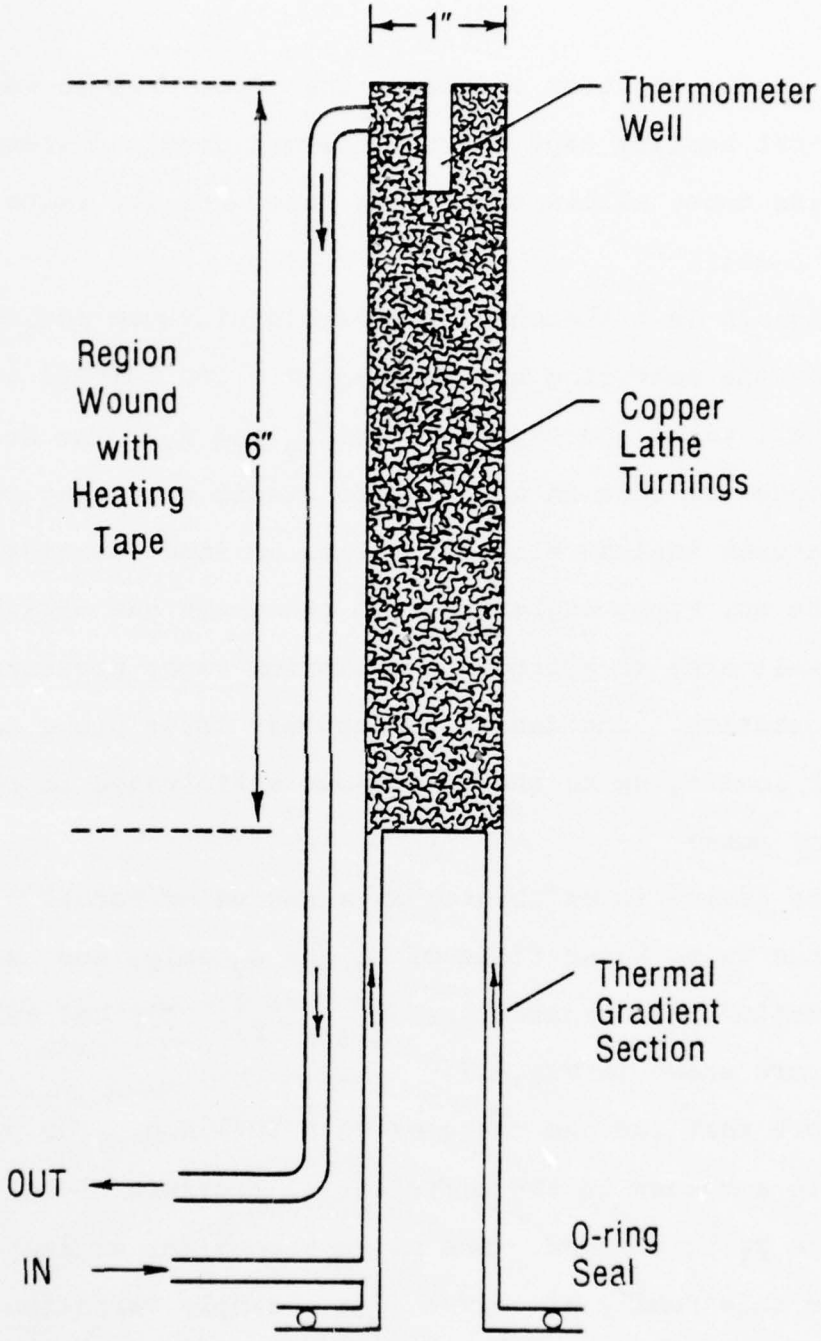


Figure 15. Chamber for O_2 Removal

sketch of the reaction chamber. The upper half is wound with electrical heating tape and the thermal gradient along the stainless tubes allows the O-ring below and the valve beyond it to run cool.

Fig. 16 is a sketch of the liquid nitrogen cooled trap shown in the measuring system diagram. Its purpose is to remove all gases and vapors except O_2 and N_2. The design anticipates flowing in addition to static operating conditions. Its features include all cold walls, an input section difficult to choke up, right angle bends to encourage gas mixing, and a large wall area to approach equilibrium vapor pressures in the output section. The design concept may later prove to be useful for scaling up to the full flows anticipated in the main delivery tube.

The device is calibrated at a series of normal operating pressures using known flows of N_2 and O_2 only, and hence a known ratio of concentrations $[O_2]/[N_2]$. Typical calibration curves are shown in Fig. 17.

Note that for the cases of zero $[O_2]$, i.e., for pure N_2, there is a change in the differential pressure ΔP as the input pressure P_1 is changed. One might expect (or at least hope) to see for this family of curves just a simple variation in slope and a common intersection at the origin. The reason for the lateral displacements measured probably results from differences in viscous drag on the N_2 flow between the hot chamber filled

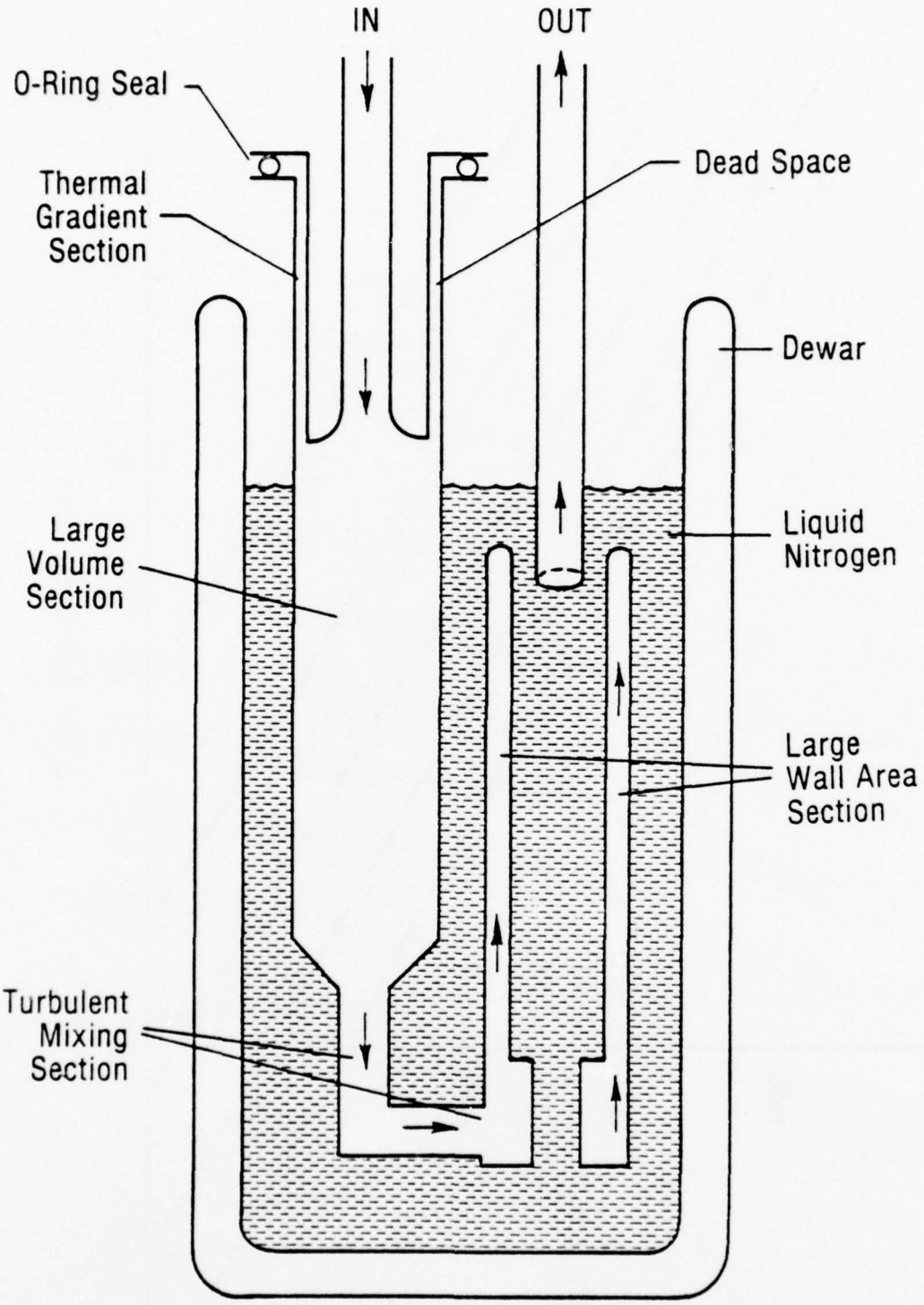


Figure 16. High-Capacity Fast Flow Trap

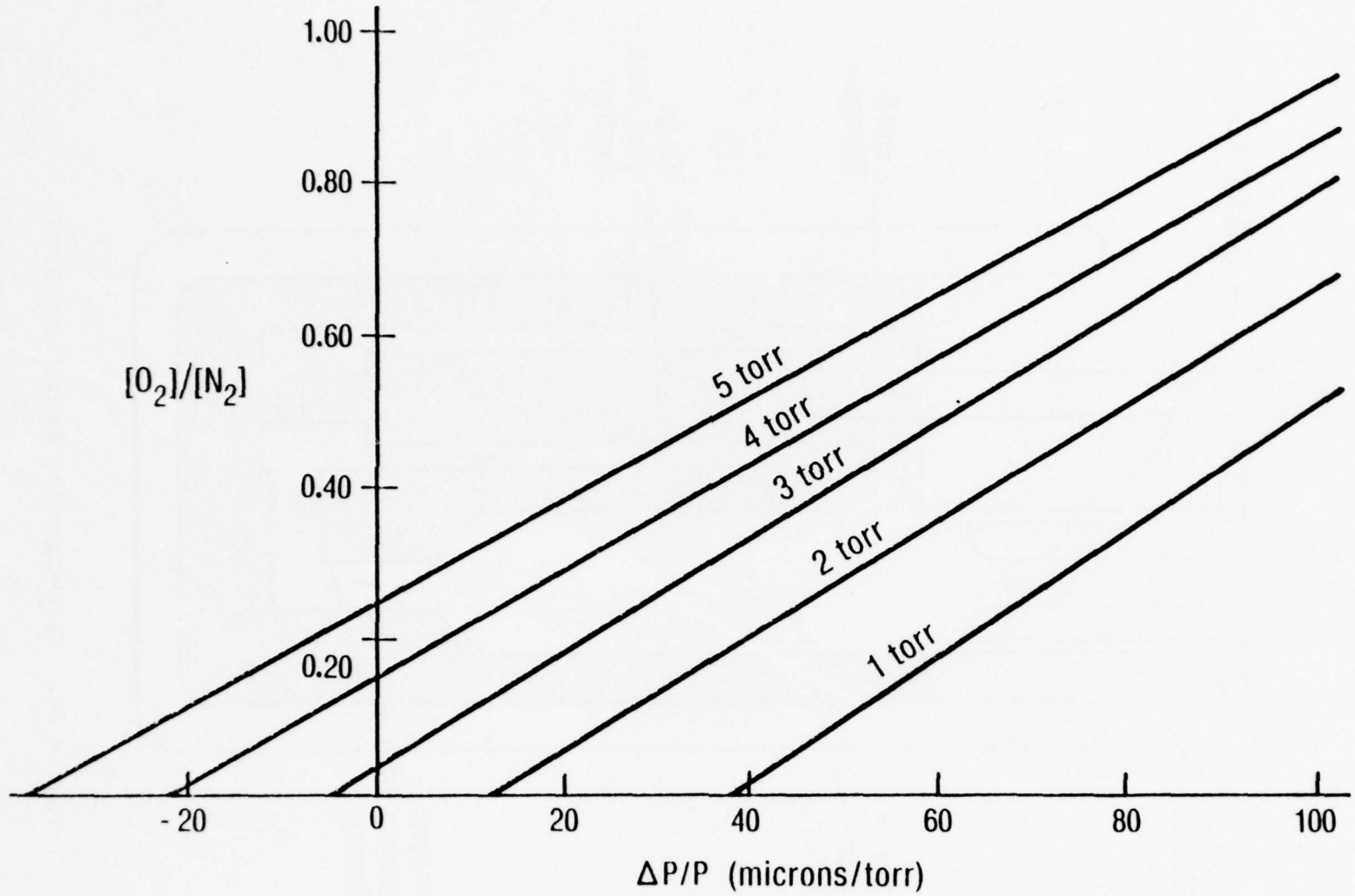


Figure 17. Calibration Curves for O_2 Trap

with chips and the cold chamber empty. It would probably be worthwhile to substitute a second identically heated chamber filled with chemically inert stainless or gold plated copper turnings in place of the present cold and empty reference chamber.

3. MEASUREMENT OF TOTAL SYSTEM FLOW

The N_2 input flow to the system is measured by flowmeters carefully calibrated against a volume-displaced-per-unit-time standard. Because no N_2 is generated or lost in the system, the flow of N_2 is completely known. Since, as explained immediately above, the ratio of concentrations $[O_2]/[N_2]$ is known at the output, the exit flow of O_2 is also known. From the sum of these two flows, the diameter of the tube,and the pressure at the exit port,a minimum velocity can be calculated which differs slightly from the real velocity because a small component of trapable vapors,such as Br_2, H_2O,and H_2O_2,have been omitted from the calculation.

Thus an independent measurement of the flow of these condensible vapors must be made before the total flow can be measured rather than bounded. This measurement was not attempted in the present study. Its absence contributes a small but definite error to the present measurements of total flow and thereby to the concentration of $O_2(^1\Delta)$.

SECTION V

GENERATOR OPERATION

The operation of the $O_2(^1\Delta)$ generator has been divided into three parts: the input of reactants, the conditions during the operation of the generator, and the output of the products.

1. INPUT OF REACTANTS

The chemical inputs to the generator consist of bromine vapor, hydrogen peroxide-sodium hydroxide solution, and inert carrier gas (nitrogen). The operation of the generator will be described in terms of each of these.

In order to regulate the flow of bromine vapor, it was necessary to place the bromine reservoir in a water bath which was equipped with facilities for stirring and heating. By maintaining the bath temperature at about 40°C, it was possible to eliminate the earlier problem of the liquid bromine freezing when exposed to the near vacuum of the generator. A stainless steel needle value provides control of the amount of bromine deposited on the cold band of the dewar.

Several different designs were tested in order to find the optimum method of directing the bromine vapor onto the cold band of the rotating dewar. The first device consisted of a Teflon fitting having two parallel vertical slits 1/2 inch in length and 1/4 inch apart. It was attached to the end of the glass bromine inlet tube. This fitting deposited on the dewar a 1 inch wide band of bromine having diffuse edges. Because of the quantity of bromine later found in the traps, it was felt that considerable bromine was escaping condensation on the

cold band. A second director was fabricated which could be placed closer to the cold band and had a horizontal slit 1 inch wide and 1/8 inch high. This second director also matched the cylindrical curve of the dewar. This device deposited a well-defined band of bromine which was, however, too narrow. The third and final director was similar to the second but the slit was enlarged vertically so that the device now became a "horn", again with the mouth having a curvature which matched the dewar. This director worked well and has been used in all subsequent runs with the generator. In general, it can be said that the technique for laying down a layer of bromine on the cold rotating dewar has been well worked out.

In Part One, the peroxide solution typically consists of 30% H_2O_2 that has been made strongly basic by the addition of NaOH. The solutions used were usually 12% NaOH by weight. This concentration of base was chosen from the results of earlier experiments at atmospheric pressure which produced a maximum intensity of red dimol radiation. This choice of base concentration was further tested at low pressure in the generator, where it was found that any significant decrease in the concentration of NaOH resulted in a decrease in the $O_2(^1\Delta)$ concentration. This effect of NaOH concentration has not been fully explored by a sequence of accurate measurements under strictly controlled conditions.

The preparation of the peroxide solutions was carried out with due caution, because it is well known that base catalyzes the decomposition of H_2O_2. It was found that pre-chilling the H_2O_2 solution to about 5°C, followed by slow addition of the NaOH pellets with constant stirring, allowed the solutions to be prepared

without noticable decompositon. In addition, a solution stored at slightly below room temperature was found to keep for hours or even days. An alternative and often effective way of preparing the solution was by predissolving the NaOH pellets in a small amount of distilled water. This solution was then cooled to remove the considerable heat of solution of the solid NaOH and was then added to the H_2O_2. The resulting peroxide solution was only slightly more dilute than that prepared by the previous method.

A problem which developed early in the generator operating procedures was the clogging of the small (0.013"dia.) peroxide injection orifice. This blockage was caused by two processes: the freezing of the liquid in the tube, and the blockage of the orifice by precipitated NaOH particles. Both problems were relieved by the addition of a manually actuated scraper inside the stainless steel tube. This was moved up and down to clear the nozzle when necessary. In practice it was found that once the flow was started the orifice tended to remain clear so that the use of the scraper was required mainly at re-starts and seldom during the course of a run.

Numerous experiments have been carried out to approach an optimum peroxide nozzle configuration. The first design consisted simply of a single hole drilled radially through the wall of the stainless steel peroxide inlet tube. The hole was level with and about 1 inch away from the cold band of the rotating dewar. Various hole sizes were tried in this design, ranging from 0.013 inch to 0.050 inch dia. A second type of peroxide nozzle design consisted of four holes through the inlet tube wall spaced vertically with about

3/8 inch separation. Several of these tubes were made with equal size holes or with diameters increasing down the tube. These experiments lead us back to the use of a single 0.013 inch dia. hole for the peroxide nozzle. Other designs were not as effective because the H_2O_2 input was well in excess of the amount of bromine that could be put on the cold band and thus much of the peroxide was wasted.

An attempt was made to decrease the flow velocity of the peroxide jet by aspirating a partial vacuum above the peroxide reservoir. This caused the solution in the reservoir to bubble vigorously. The method was subsequently abandoned because the reagent became difficult to control.

We also examined the effect on the output concentration of $O_2(^1\Delta)$ of atomizing the peroxide solution prior to its reaction with bromine. The scheme (based on a successful industrial atomizer) consisted of running a stream of the liquid to be atomized down the outside of a hollow tube, near the bottom of which was a small horizontal slit 0.5 inch wide by 0.015 inch high. Carrier gas was blown into the top of the tube, and at atmospheric pressures the liquid running down over the slit was very well atomized. In low pressure tests, this atomizer worked down to about 20 torr, but below that pressure the effectiveness decreased until at 2 torr the liquid ran around instead of across the atomizing slit.

A slightly different approach to atomization was then tried. The slit in the carrier gas tube was cut in the vertical rather than the horizontal plane and a thin curved metal tab was attached

to the tube. This tab guided the stream of peroxide solution from a nearby standard 1-hole peroxide nozzle across the atomizing slit. When carefully aimed, the peroxide jet was efficiently atomized even at pressures as low as one torr. Atomization had no measurable effect, however, on the output concentration of $O_2(^1\Delta)$, so that for subsequent runs we again used the simpler 1-hole, 0.013"dia. peroxide nozzle.

Other alterations were also made in the chemistry of the peroxide solution. The concentration of H_2O_2 was varied as well as concentration of NaOH, and KO_2 was added to the H_2O_2 solution. Changing the H_2O_2 concentration was the single experiment most productive in increasing the $O_2(^1\Delta)$ output concentration. Varying the H_2O_2 concentration between 10 and 50% did not significantly effect the output. The use of 90% peroxide, however, caused a substantial increase in the $O_2(^1\Delta)$ concentration and gave the best yields of all of our experiments to date. The effects of changes in the NaOH were examined briefly. It appears that a substantial decrease in NaOH concentration (by about 50%) causes a decrease in the $^1\Delta$ output. The optimum NaOH concentration for a given H_2O_2 concentration has not yet been accurately determined.

The addition of potassium superoxide (KO_2) gave a slightly higher yield of $O_2(^1\Delta)$. This is attributed to the resulting increase in the effective H_2O_2 concentration caused by the superoxide ion.

2. REACTION CONDITIONS

The effect of changes in some of the generator parameters was investigated in order to find the optimum running conditions.

Several refrigerants were tried in the rotating dewar. Experiments showed that ℓN_2 was not an effective coolant because the reaction by-products froze on the dewar and did not fall into the gravity trap. The frozen by-products were also difficult to remove mechanically from the dewar. The refilling of the dewar and the rapid evaporation of the ℓN_2 presented additional problems.

In one run, an ice-water/salt slurry ($-15^{o}C$) was used as the refrigerant in the dewar. In this case, however, the bromine did not deposit preferentially on the rotating cold band but either deposited in the much colder gravity trap or was pumped away.

The next refrigerant used was ethanol/dry ice. This slurry was cold enough to freeze out the bromine on the cold band of the dewar while allowing the convenient removal of the by products from the cold band. Substitution of acetone for ethanol gave a still better refrigerant, because while the ethanol became very viscous at dry ice temperature, the acetone showed almost no viscosity increase. Benchtop tests also showed the acetone/dry ice refrigerant to be more effective in terms of greater heat flow than the ethanol slurry. Acetone/ dry ice was used in all subsequent experiments. With favorable reaction conditions having been determined by preliminary tests, a number of experimental runs were completed, typically in the following manner.

The rotating dewar was filled with acetone/dry ice mixture and all other down-stream traps filled with ℓN_2. The gravity-trap was

also placed into a ℓN_2 dewar. The temperature in the bromine reservoir bath was established at 40°C, and the control valve on the bromine flow opened so that a bromine band was deposited on the dewar which was rotating at about 10 pm. The H_2O_2 solution was then added, and a vigorous reaction immediately occured. The peroxide jet was adjusted to impinge on the frozen bromine band in such a way that the region of the rotating dewar leaving the reactor zone was covered with white foam, with the absence of red color indicating complete reaction of the bromine. During the course of the reaction, the external glass wall directly behind the peroxide nozzle would become heavily spattered with liquid reaction by-products, which would wash down into the gravity trap. Because of this washing action, the visibility through the outside wall remained good. About 1" past the reactor zone the scraper would remove the remaining white foamy slurry, forcing it to fall into the gravity trap. When properly adjusted, a sharp-edged red band of frozen Br_2 could be seen moving into the reactor zone, while a clean stainless steel surface would emerge from behind the scraper. After rotation of another 180°, bromine would be re-deposited on the band. Once these conditions were established (usually within a minute), the generator would continue to operate with a minimum of attention and would run until one of the reactants ran out (usually the 250 ml fill of H_2O_2 solution). The generator has been run for 45 min. continuously in this fashion and presumably could be run longer if larger charges of peroxide solution are used.

3. OUTPUT OF PRODUCTS

The reaction products are assumed to be essentially O_2, H_2O, and NaBr. In addition, unreacted Br_2, H_2O_2, and NaOH are present. The trapping of the reaction by-products is carried out in large part by the gravity trap, which catches the bulk of the unreacted reagents, water, and salt. The effluent gas stream consists of carrier gas, O_2, H_2O vapor, H_2O_2 vapor, and Br_2. In addition, small amounts of solid by-products are carried in the gas stream.

The dead-end gravity trap has proven to be a useful concept and in general was found to perform efficiently. Some of the by-products, however, tended to accumulate near the top of that trap, eventually freezing and blocking the trap before they could reach the bottom. The trap was then modified by enlarging its input window and at the same time lowering the level of the ℓN_2 refrigerant around it, thus eliminating this problem.

The first downstream cold-finger trap was constructed of heavy-wall glass and maintained at ethanol/dry ice temperature. After several runs a severe crack developed in the outer wall, possibly due to thermal stress. This trap was then replaced by the stainless steel cross-tube trap mentioned previously. Examination of this trap after a run showed ice and frozen bromine on the input side, and almost no ice but still some frozen bromine on the output side. The trapping of bromine vapors, even in ℓN_2, has been a problem due to the large volume flows and high pumping rates under which the generator operates.

SECTION VI

RESULTS - PART ONE

1. REVIEW OF RESULTS

a. Chemistry

Preliminary experiments under atmospheric conditions showed an optimum yield of $O_2(^1\Delta)$ from the reactions of Br_2 with H_2O_2 in concentrated highly basic solution. This reaction is controllable under low pressure conditions, as we demonstrated, by freezing the Br_2. A modification, the reaction between hypobromite and peroxide, proceeds well under acidic and possibly also under neutral conditions. It likewise demonstrated promise of practicality under low pressure conditions.

b. Chemical Engineering

A low pressure reactor was designed, built, and tested. Its engineering performance met our expectations in all regards and especially in the ability to run for indefinitely long times.

c. Total Oxygen

A scheme was devised and equipment built for the measurement of the concentration of oxygen diluted by other vapors and in rapid flow at low pressures. This O_2 measurement apparatus was finished only near the termination of this work. The recent measurements made with it do, however, make possible plausible corrections to the earlier flow measurements made using

cruder equipment. On that basis, we estimate that total oxygen flows from the generator have been as large as 1 standard liter per minute while flowing at 1,000 cm/sec through a 5 cm diameter tube. This is equivalent to a 0.1 torr partial pressure of oxygen under those flow conditions. Since much larger flows have been observed for short times, it seems that a generator of this size is indeed large enough to meet the present 1 torr design goal.

d. Excited Oxygen

Three methods for measuring evolved $O_2(^1\Delta)$ were tried in the laboratory: first, direct photometric comparison with NO-O fluorescence in the same container; second, a similar comparison with $O_2(^1\Delta)$ as made by a microwave generator; and finally, our new concept of a calibrated piston source. Since the last was superior in accuracy among the three, easier to use, and essentially as sensitive, it was adopted as the laboratory standard.

In combination with the oxygen flow device, the piston source was used to measure the ratio of concentrations $[O_2(^1\Delta)]/[O_2]$. For the best results obtained to date, this ratio was not less than 8% and probably did not exceed 15%.

e. Impurities

The equipment developed to date for the removal of impurities has consisted of a series of progressively improved cryogenic traps. The design of such traps is complicated by five considerations in a complex combination; the main stream flow is a high velocity, the pressure is low, the impurity content

is large, employment of too low temperatures may deactivate $O_2(^1\Delta)$, and for the same reason, non-trapping wall area should be a minimum.

Several multiple transverse-tube traps operating at dry ice temperatures were built and tested in this service. Examination of deposits on the wall following a run showed very effective removal of H_2O and H_2O_2 vapors. Particulates likewise were well trapped. Much Br_2 was also retained, but a non-trivial fraction was still in evidence at the exit end. Extrapolation of these results encourages us to think that a somewhat larger trap of similar design will remove Br_2 when it is operated at a lower temperature.

2. SUMMARY

We have had good success in the design of cryogenic traps to remove H_2O_2, H_2O, and particulates from the fast flowing output stream in spite of the low pressure and substantial quantity to be removed. The removal of Br_2 is a problem about which we do not yet have enough information, but which we think may yield to similar trap designs based on lower temperatures as yet unexplored.

SECTION VII

INTRODUCTION - PART TWO

1. PROGRAM OBJECTIVES

The objectives of the second phase of the "Chemical Generation of Excited Oxygen" research program were to characterize the performance of the generator by varying those parameters that appear to have a substantial effect on the yield of $O_2(^1\Delta)$. These included the concentrations of reactants, pH of reactants, flow rates, and mixing configurations. In addition, more effective techniques for trapping impurities from the generator output were to be investigated.

2. PROGRAM RESULTS

The work for the period of the project included in Part Two involved the following:

(a) Design and construction of modifications to generator system (including improving bromine and peroxide handling facilities, installation of ℓN_2 PMT cooler, construction of spectrometer-PMT detection assembly, developing total oxygen techniques and design and construction of fast-flow cryogenic trap for output impurities.

(b) Calibration and testing of $O_2(^1\Delta)$ detection system.

(c) Design, testing and evaluating of several mixing schemes (including liquid-liquid mixers and improved H_2O_2 atomizers.)

(d) Discovery and testing of new group of $O_2(^1\Delta)$ producing solids.

SECTION VIII

GENERATOR MODIFICATIONS

1. UPGRADING OF BROMINE AND PEROXIDE HANDLING EQUIPMENT

Due to the extreme corrosive nature of the reagents used in the generator, as much as possible of the halogen and peroxide handling equipment was replaced by glass, Teflon, and stainless steel parts. A glass and Teflon metering valve with a Viton O-ring was found to stand up well to gaseous and liquid bromine vapor. Teflon tubing as well as Teflon connectors and Teflon-lined ultra-torr connectors were used exclusively for the bromine connections. Stainless steel was acceptable for the 90% h_2O_2-base solutions, although it was also noted that acidic H_2O_2 solutions reacted violently with stainless steel.

2. PHOTOMULTIPLIER TUBE COOLER

In order to optimize the signal-to-noise ratio (S/N) of the phototube (RAC 7102, S-1), a stable low temperature photomultiplier tube (PMT) cooler was purchased (Products for Research TE-176) which is capable of operations to -100°C with cold nitrogen gas. Under these conditions, the dark current from the tube (cathode at 1000 V) was reduced below 10^{-14} amp.

3. PHOTOMULTIPLIER-DETECTION SYSTEM

As described in Section IX below, the detection system consisted of a spectrometer and a cooled PMT. The spectrometer is a Jarrell-Ash 0.5 meter Ebert type with f/8.6 optics operating in the second order. Because of the size of the ℓN_2 cooled PMT housing and the close spacing of the inlet and exit slits of the spectrometer, the spectrometer had to be mounted such that its main optical axis was perpendicular to the measuring tube-PMT axis. This required the construction of a light-tight box with two 45° mirrors on three-point adjustable screw mounts. A silicon filter was mounted in front of the tube to minimize the white light interference, and the PMT was cooled to -100°C with liquid nitrogen.

4. OXYGEN MEASURING TECHNIQUE

The original concept for measuring the total oxygen, that of the oxygen bridge, was found to present several problems, the principle two being: (1) slow response time (several minutes per reading) and (2) inconsistencies in calibration readings. The second point indicated that more time would have to be spent in determining the optimum temperatures for oxidation and reduction of the copper as well as the total volume of oxygen and hydrogen required for optimum operation. Time limitations prevented further exploration of these problems, therefore a different method was used to measure the oxygen

pressure. This consisted of measuring the pressure rise at the onset of the reaction using a Baratron capacitance manometer gage in the absolute pressure measuring configuration.

To do this, one side of the gauge was pumped down to the lowest pressure obtainable by the system (several microns) and then sealed off. Since the total pressure would be in the 5 torr range and only the difference was measured, this value of "zero" pressure was satisfactory. The other side of the Baratron was connected to the flow system at the end of the measuring tube, and a final ℓN_2 trap was inserted in front of the Baratron.

The oxygen pressure was measured as follows: the carrier gas (nitrogen) pressure was set at the beginning of the run, usually at 4.0 torr. This was not changed during the course of the reaction. The reagents (H_2O_2 and Br_2) were then introduced into the generator one at a time and in such a way as not to start the reaction, and the pressure rise due to each was noted. With this pressure as a "baseline", the H_2O_2 was directed onto the target. The ensuing pressure rise at the onset of the reaction was attributed mostly to oxygen production. The response time for this method was less than 1 sec. For increased sensitivity, both sides of the Baratron were equalized after setting the carrier flow, thus reducing the baseline to zero. The pressure rise due to the reaction could then be read on a more sensitive scale.

This technique for measuring the total O_2 pressure was also checked by using a "batch" method in which a sample of the gas flow was admitted into an evacuated sample bulb during the run and correlated with the recording of the real-time pressure rise. After completion of the run, the pressure in the sample bulb was measured (again using the Baratron) and then remeasured after placing the tip of the bulb in an acetone-dry ice bath. The pressure drop corresponds to the vapor pressure of the impurities, consisting of Br_2, H_2O, H_2O_2, and possible traces of other compounds. Since the original nitrogen pressure was known (and assuming the pumping speed did not change with the onset of the reaction), the partial pressure of O_2 in the bulb could then be determined. The small volume decrease upon opening the sample bulb to the Baratron could be determined with nitrogen and the temperature effect caused by the cooling would have negligible effect due to the small area (~several cm^2) that was actually cooled. The batch method was tested for the bromine experiment and for solid salt experiments. and in both cases the total O_2 determined by the two techniques agreed within 15%.

5. FAST FLOW CRYOGENIC TRAP

In order to more efficiently trap impurities from the output flow of the generator, a fast flow stainless steel cryogenic trap was built (Fig. 18). The trap is essentially a

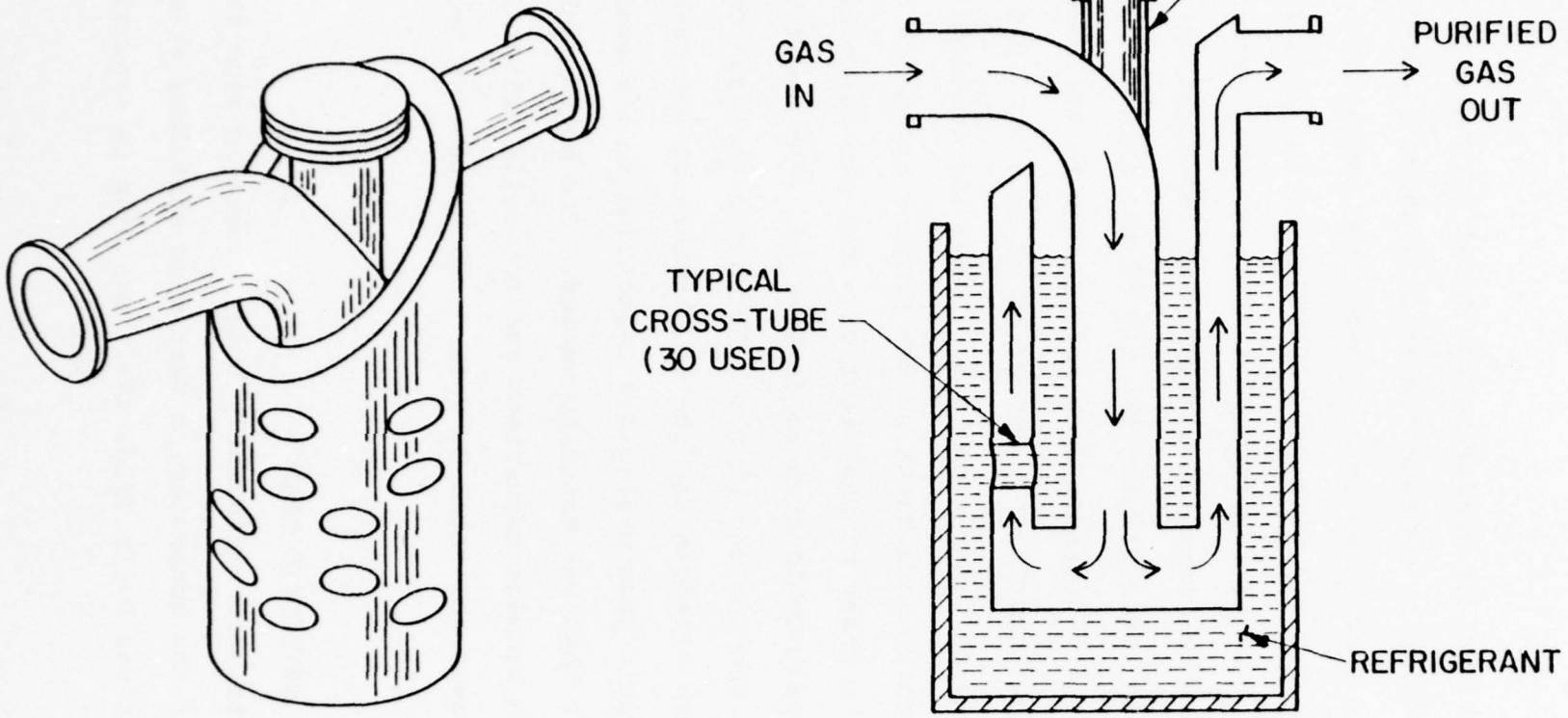


Figure 18. Fast Flow Cryogenic Trap

two stage device. The first stage consists of a large diameter straight tube which serves to remove the easily trappable impurities (water, hydrogen peroxide, etc.) without clogging the trap. The clogging was found to be a problem with traps of earlier design. The second stage consists of a region crossed by numerous tubes which provides a large surface area of cold wall for removing the halogen from the gas flow. These tubes also serve to disrupt the laminar flow. The trap features a removable plug to facilitate cleaning.

SECTION IX

CALIBRATION AND TESTING OF DETECTOR SYSTEM

An initial attempt to use a spike filter (λ_{center} = 1.282μm, ½BW = 14nm) and a silicon filter was unsuccessful due to a very large wing on the blue side of the spike filter. This apparently resulted from the rapid increase in the sensitivity curve of the PMT (RCA 7102, S-1 surface), which rises many orders of magnitude from 1.3 μm to 1.0 μm. In addition, the silicon filter also starts transmitting just to the blue side of 1.0μm and the combination of the two effects results in the peak sensitivity of the detection system being at 1.05μm, with the area under this part of the transmission curve being many times greater than that under the pass-band of the spike filter. This approach therefore had to be abandoned in favor of a spectrometer-PMT system.

The new spectrometer-PMT system (Section VIII.3) was checked against a tungsten source and the ratio of the photocurrent at λ at maximum sensitivity to λ at 1.27μm, ($I_{max}/I_{1.27}$), was found to be ~300.

Due to intrinsic white light scattering, the ratio of the signal at 1.27μm to that at 1.40μm was found to be ~3. The signal at 1.4μm represents that due strictly to this scattering (mostly the 1.05μm component), as the PMT has virtually no sensitivity at the 1.4μm wavelength. The $I_{1.4}$ is therefore

used as the "zero" level for all readings and is subtracted from each measured number. The actual dark current (shutter closed) is very small, being typically ~1×10^{-13}A (at -100°C, 1200 V). Wavelength calibration of the spectrometer was made in the first order against a He-Ne laser at 6328Å, with a 25μ slitwidth.

SECTION X

REACTION SCHEMES

1. LIQUID-LIQUID REACTION

Preliminary work was carried out with Dr. M. Steinberg to examine possible methods of controlling a liquid-liquid Br_2-H_2O_2 reaction. A system to examine qualitatively the mixing time for the reaction

$$Br_2 + 2OH^- \rightarrow OBr^- + Br^- + H_2O$$

was built and operated and revealed that several seconds are needed for the formation of the OBr^- ion. The subsequent reaction of the OBr^- solution with H_2O_2 gave only weak chemiluminescence, possibly because the OBr^- decomposes before the H_2O_2 has time to react.

To further explore this reaction, several liquid-liquid mixing schemes were examined. In a preliminary setup, a T-mixer was constructed out of Teflon and was connected to the reagent reservoirs by glass capillary tubing (1.5 mm i.d.). Metering valves of glass and Teflon were used to control the flows, and a laboratory sink aspirator was used to provide the vacuum. This system is shown in Fig. 19. The initial run showed this T-mixing concept to be a workable one, with red dimol radiation being observed at the mixer output.

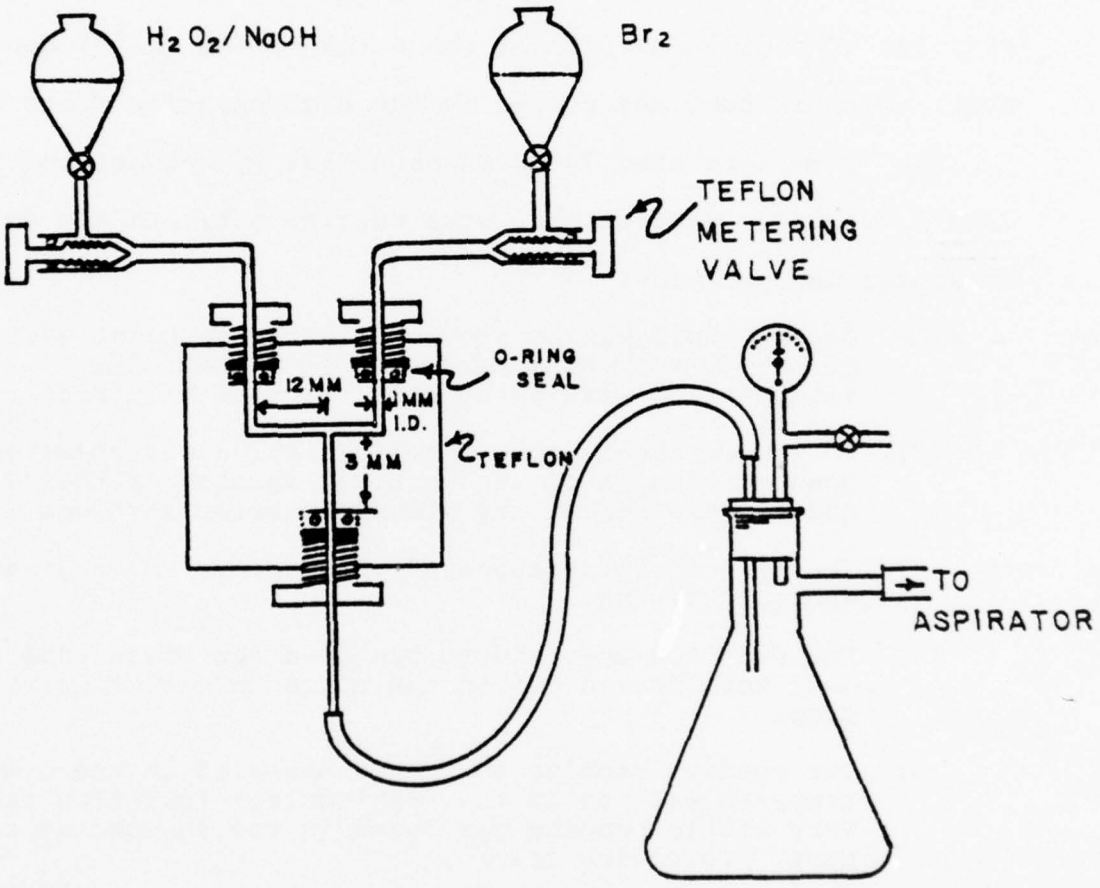


Figure 19. Preliminary Liquid-Liquid "Tee" Mixing System

Due to the Teflon construction of this first mixer, however, the reaction occurring at the point of mixing could not be seen, and so another mixer was built. In this second device, the T was made from glass capillary tubing (1.5 mm i.d.), as shown in Fig. 20. The mixer output was connected to the $O_2(^1\Delta)$ generator, which in turn was pumped by the high-capacity Roots pump.

The "T"-mixers used 90% H_2O_2/NaOH (13% by weight) and liquid bromine. Several runs were carried out, and the following observations were made:

(1) Fairly rapid mixing occurred in the vertical section of the T, with most of the red bromine color disappearing within the first 1 cm after mixing.

(2) In the darkened room, dimol radiation was observed down the length of the vertical section of the "T" and disappeared at the glass expansion section.

(3) The mixing region appeared very foamy, which greatly enhanced mixing.

(4) The reaction by-products ran down the glass tube and most were frozen out in the nitrogen cooled gravity trap.

(5) The reddish bromine color was observed in the gravity trap, as well as in the (ℓN_2-cooled) full-flow trap. Very little bromine was found in the ℓN_2 cooled fore-pump protection trap.

(6) Approximately 15 to 20 ml of H_2O_2/NaOH solution was used per ml bromine liquid, this quantity being consumed in about ½ minute.

(7) The total O_2 output under conditions in (6) above was about 1 torr, with a flow rate of ~2000 cm/sec through 5 cm i.d. tubing (no carrier gas was used).

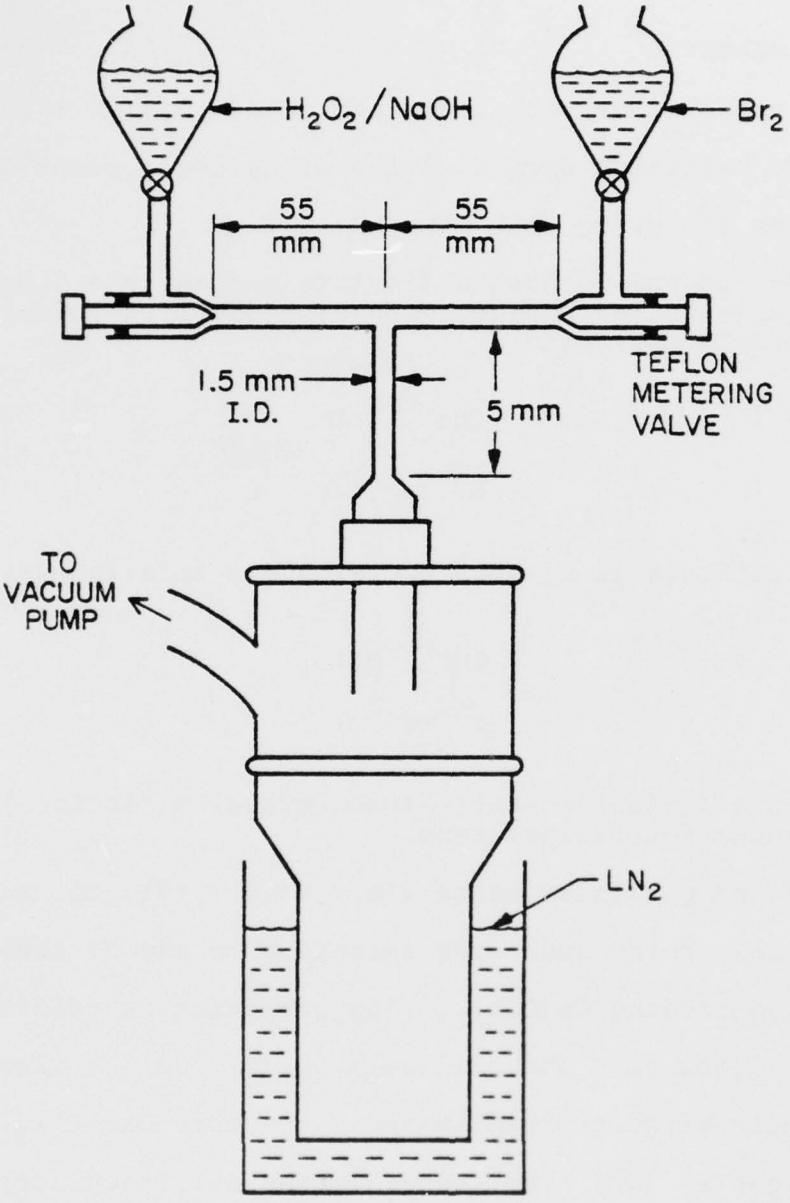
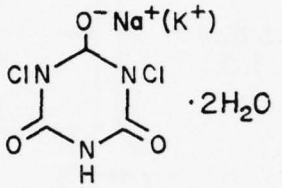


Figure 20. Liquid-Liquid Mixing System

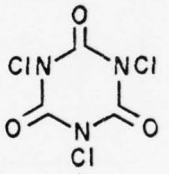
2. SOLID REAGENTS

A new class of dry chemicals was found to give extremely intense red radiation upon addition of hydrogen peroxide. This included the following (Ref. 9):

(a) Sodium and potassium dichloroisocyanurate dihydrate (also called sodium, potassium dichloro triazine-s-trione dihydrate),



(b) Trichloro isocyanurate (trichloro triazine-s-trione),



(c) [mono-(trichloro-tetra-(monopotassium dichloro)] penta-s-triazinetrione.

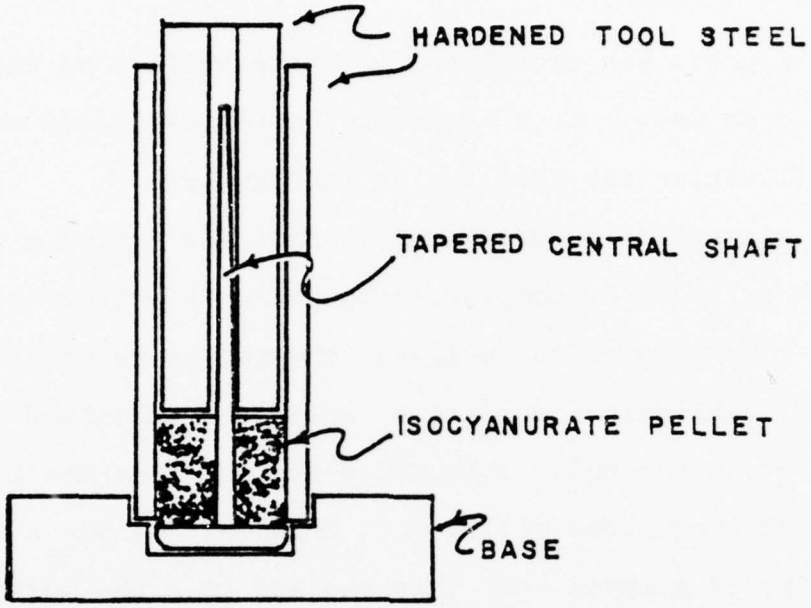
The sodium and potassium salts ((a) above) yield the most intense red radiation, being much more intense than any of the hypochlorites, including $Ca(OCl)_2$. The radiation is readily seen with room lights on. The chemicals in (b) and (c) also give significantly brighter chemiluminescence than $Ca(OCl)_2$, although not as bright as (a). The (non-chlorinated) isocyanuric acid gives no radiation. The pH of the hydrogen peroxide apparently has little effect on the intensity of the red radiation, but the more concentrated hydrogen peroxide does appear to produce more intense chemiluminescence.

A press was fabriacted by which pellets of these chemicals could be made. This technique was investigated as a method of facilitating the handling of the powders.

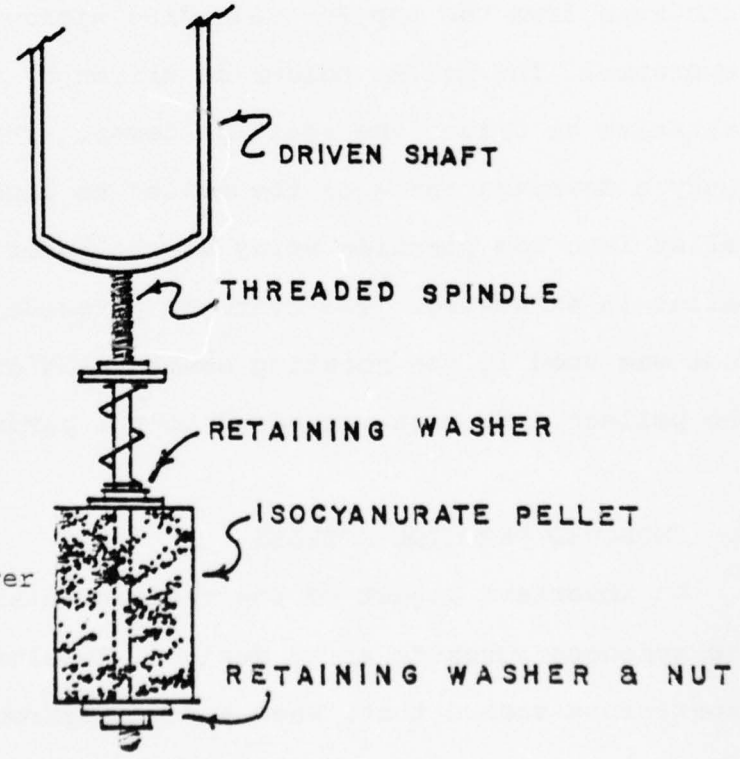
The pellet press, shown in Fig. 21a, forms a 2 inch by 1 inch cylinder of compressed powder with a 3/16 inch hole through the long axis of the pellet. The pellet is mounted on a holder (Fig. 21b) which consists of a 1½ inch stainless steel tube sealed at one end. Into the center of this end is connected a 3 inch long piece of 1/8 inch threaded stainless steel rod. A spring is slipped over this rod and then the pellet is loaded onto the shaft, with a washer and nut holding it in place. This assembly is mounted in place of the rotating dewar and can be withdrawn from the top for reloading without disassembly of the generator. The pellet holder is driven by the same worm gear mechanism as drives the rotating dewar. The spring serves to apply a downward force on the pellet to constantly feed the pellet into the peroxide spray as the lower portion of the pellet is exhausted. The hydrogen peroxide spray configuration that was used in the rotating dewar reaction was also used with the pellets. No base was added to the peroxide.

3. IMPROVED PEROXIDE NOZZLES

An important aspect of the reactant mixing problem concerned the hydrogen peroxide spray design. Results from several experiments showed that, when a given hydrogen peroxide flow was



(a) Pellet Press

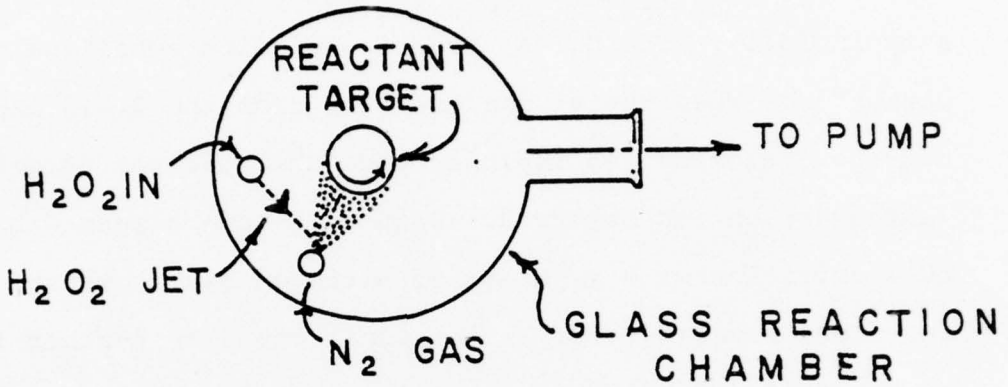


(b) Pellet Holder and Driver

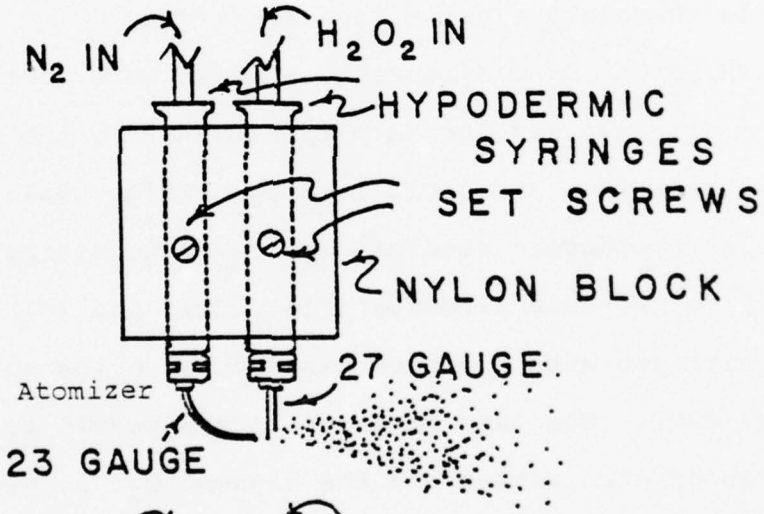
Figure 21. Pellet Press and Pellet Holder/Driver

highly atomized before being allowed to react with the bromine or triazine salt, the partial pressure of $O_2(^1\Delta)$ increased substantially. The $O_2(^1\Delta)$ signal was quite sensitive to this parameter. When the stream emerging from the 0.013 inch hydrogen peroxide jet impinged upon the reactant target, only weak emission was observed. When this same stream was broken up by atomization with a stream of nitrogen gas, however, the signal increased several fold. This signal could be further improved by carefully adjusting the atomizing conditions, but these subtle changes are not fully understood.

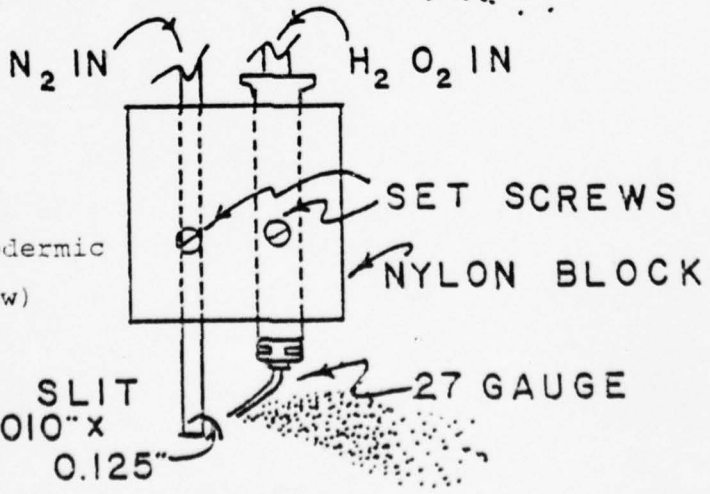
The atomizer configurations which were tested included: (a) a nitrogen gas stream perpendicular to the hydrogen peroxide jet stream from the 0.013 inch hold (Fig. 22a); (b) two perpendicular hypodermic needles, one carrying nitrogen and the other carrying hydrogen peroxide (Fig. 22b); and (c) a slit opening for nitrogen with hydrogen peroxide spraying across the slit (Fig. 22c). The last configuration appeared to give the highest degree of atomization and the highest $O_2(^1\Delta)$ signals.



(a) Peroxide Atomizer (top view)



(b) Peroxide Hypodermic Atomizer (side view)



(c) Peroxide Slit-Hypodermic Atomizer (side view)

Figure 22. Peroxide Atomizers

SECTION XI

RESULTS - PART TWO

1. PRELIMINARY RESULTS

Preliminary results were obtained from the following reaction schemes (as described in Section X): (1) liquid bromine with 90% H_2O_2-NaOH solution (13% by weight), (2) sodium dichloroisocyanurate dihydrate with 90% H_2O_2, (3) trichloro-isocyanurate with 90% H_2O_2, and (4) $Ca(OCl)_2$ with 90% H_2O_2. In addition, a run with $O_2(^1\Delta)$ generated by microwave discharge was also carried out.

These runs were for the most part carried out with the large Roots pump on, such that the pumping speed was 2000 cm/sec. Nitrogen gas was also added in several experiments. For these preliminary tests, the fast flow trap was not used.

The first run was made with the microwave discharge, and with the nominal 80 watt output only a small signal at 1.27μm was obtained (output P_{O_2}=1.5 torr optimum). The signal was ~$1x10^{-13}$ Å, which was only several times the "zero" level. No attempt was made to remove O atoms from the flow. The signal was not strong enough to attempt any line width measurement.

The liquid bromine-basic 90% hydrogen peroxide reactor typically produced an O_2 pressure of from 2 to 1 torr, with the larger number apparently representing the limit of the

input flow of reactants. This reaction gave a signal that was slightly better than that from the microwave discharge. Again no attempt was made to trap bromine or other by-products other than by the gravity trap. When nitrogen gas was added during the course of the run there was little effect on the results.

For the three powder-peroxide reactions, the 90% hydrogen peroxide was added by the same system used in the rotating drum experiments. Of the three, the sodium salt gave the most encouraging results, with a slightly higher $O_2(^1\Delta)$ signal and an apparently faster reaction. The total O_2 pressure resulting from the reaction was about 2 torr. It appeared that the area of the solid exposed to the hdrogen peroxide limited the reaction, as increased hydrogen peroxide did not increase the output pressure. The red radiation from this reaction was very intense, with the whole outside of the pellet being engulfed in a bright red glow as the reaction proceeded. Upon shut down of the reactor, the pellet was found to be highly eroded, but the exposed surface was very clean and dry. The trichloro and the $Ca(OCL)_2$ salts reacted much less violently, with the trichloro salt showing almost no red radiation and a very small 1.27μm signal. A spot of red radiation was visible during the $Ca(OCL)_2$ reaction, but the apparent amount of $O_2(^1\Delta)$ produced was also small.

The role of the nitrogen carrier was examined, and it appears that a strong flow of nitrogen (5-20 torr) increased

the $O_2(^1\Delta)$ signal, perhaps by moving the gas away from the reaction zone faster. Above the upper value of this pressure, the signal decreased again. It appears, therefore, that nitrogen carrier gas is useful in the powder reactions.

The effects of variation of hydrogen peroxide concentration have also been studied. In preliminary experiments, hydrogen peroxide with concentrations of 30%, 40%, 50%, 70% and 90% were reacted with a standardized triazine pellet, and the resulting $O_2(^1\Delta)$ signal was found to increase with increasing hydrogen peroxide concentration. The 1.27μ signal increased by a factor of about 2 in going from the weak to the strong peroxide. Three different types of 50% hydrogen peroxide were also used, corresponding to different amounts and types of stabilizers used by the manufacturer, FMC Corp. These were "50% STD", "50% Tech", "50% Super-D" and 50% diluted from 90%. There appeared to be little variation in results from this parameter.

An additional triazine reaction scheme was also examined. This consisted of suspending a petri dish containing about 10 grams of the salt inside of the generator and adding 90% hydrogen peroxide to the powder. The ensuing reaction was completed within 5 to 20 seconds, depending on the rate at which the hydrogen peroxide was added, and gave the highest $O_2(^1\Delta)$ signals to date, about 100μ, with a pumping speed of 2000 cm/sec.

2. FINAL RESULTS

The optimum yields of $O_2(^1\Delta)/O_2(^3\Sigma)$ for the various solid chemicals were as follows: (1) trichlorotiazinetrion: 3±2%, (2) Na dichlorotriazonetrion·2 H_2O: 4±2%, (3) Na dichlorotriazine-trione: 5±2%, (4) $Ca(OCl)_2$ = 0% (no detectable $O_2(^1\Delta)$ emission). A decrease in these yields was noted when more dilute hydrogen peroxide was used. Using the finely powdered sodium dichlorotriazinetrion with a powder aspirator gave ~6±2%.

The best yields of $O_2(^1\Delta)/O_2(^3\Sigma)$ were achieved with the bromine-rotating dewar system. Using 90% hydrogen peroxide (25% NaOH by weight), yields of 16% were observed. This generator typically produced ~25μ of $O_2(^1\Delta)$ and 180μ of total O_2, giving $\frac{[O_2(^1\Delta)]}{[O_2(^3\Sigma)]} = \frac{25}{180-25} = 0.16$.

Experiments in which the concentration of NaOH in hydrogen peroxide was varied seemed to indicate that less than saturated solutions (25% by weight NaOH) also gave high yields, with even 12% solutions giving results similar to the saturated solutions. The lower limit was not determined.

Decreasing the strength of the hydrogen peroxide has a deleterious effect on the yield of the bromine/basic hydrogen peroxide reaction, especially below about 70% hydrogen peroxide, where the ratio decreased to half of the value obtained with 90% hydrogen peroxide (i.e. ~8%). The more dilute solutions, especially 15 to 30% hydrogen peroxide, were difficult to spray through the smallest (0.009 inch diameter) nozzles because of

freezing problems caused by the evaporation of the water and the consequent precipitation of NaOH in the colder solutions.

One attempt was made to obtain hydrogen peroxide in greater than 90% concentration. From the solid-liquid diagram of the hydrogen peroxide-water system (Ref. 10), it is possible by cooling 90% hydrogen peroxide below its freezing point (-11.5°C) to precipitate out pure hydrogen peroxide crystals, with the remaining solution becoming more dilute and reaching a minimum concentration at -56°C (corresponding to pure hydrogen peroxide crystals and 60% hydrogen peroxide solution). The purity of the hydrogen peroxide can be determined by measuring the specific gravity (90% = 1.39, 98% = 1.43) of the re-liquified peroxide. The results of one experiment using such a solution (saturated with NaOH) and bromine were indeterminate due to an unrelated problem that developed during the run, and a lack of time prevented repetition of the experiment.

The rotational speed of the dewar was also varied during the bromine experiments, with the speed being continuously variable up to 28rpm, corresponding to a maximum tangential velocity of 325 in/sec (894 cm/sec). This was found to have no noticeable effect on the reaction yield.

The temperature of the dewar was found to be important. When the dewar was kept at -77°C (with a very thick slurry of acetone-dry ice), the reaction rate decreased substantially and much of the hydrogen peroxide solution simply ran off the

surface of the frozen bromine. At the higher temperature extreme of -20°C,virtually no bromine adhered to the rotating dewar, although some $O_2(^1\Delta)$ was observed, probably due to droplet reactions on the glass and metal surfaces. The optimum temperature for the reaction on the dewar was found to be -50°C to -60°C.

One experiment was carried out in which the bromine was replaced by chlorine. Several reasons for using chlorine include the fact that this is a more reactive system and that there is some evidence (Ref. 11) that chlorine deactivates $O_2(^1\Delta)$ less than does bromine. The chlorine is much harder to trap, however, with a melting point of -101°C. Because of this point ℓN_2 was used as the refrigerant for the rotating dewar. From the physical appearance of the interaction of the peroxide and the yellow-green band of frozen chlorine, this temperature was probably colder than necessary. Using 90% hydrogen peroxide (with 25% NaOH by weight) and the same 0.009" diameter nozzle as was used previously, the yield of the reaction was about 10%. The total output, however, was ~0.7 torr of O_2. This might be a pessimistic value in that the more volatile chlorine may have been measured with the total oxygen. In addition, the rotating dewar temperature was not optimized.

In summary, the configuration which has produced the highest value for the ratio $[O_2(^1\Delta)]/[O_2(^3\Sigma)]$ was that which used the bromine and the rotating dewar. The optimum

conditions to date are: 90% hydrogen peroxide with ~25% NaOH, dewar temperature of -50°C to -60°C, N_2 carrier gas of 4 torr. This has produced ~0.2 torr of (total) O_2 at pumping conditions as defined in the Statement of Work. The ratio $[O_2(^1\Delta)]/[O_2(^3\Sigma)]$ has been measured at 16% under these conditions. The impurity concentrations have not been measured. The major impurity found in the downstream ℓN_2 trap, however, is bromine.

SECTION XII

INTRODUCTION - PART THREE

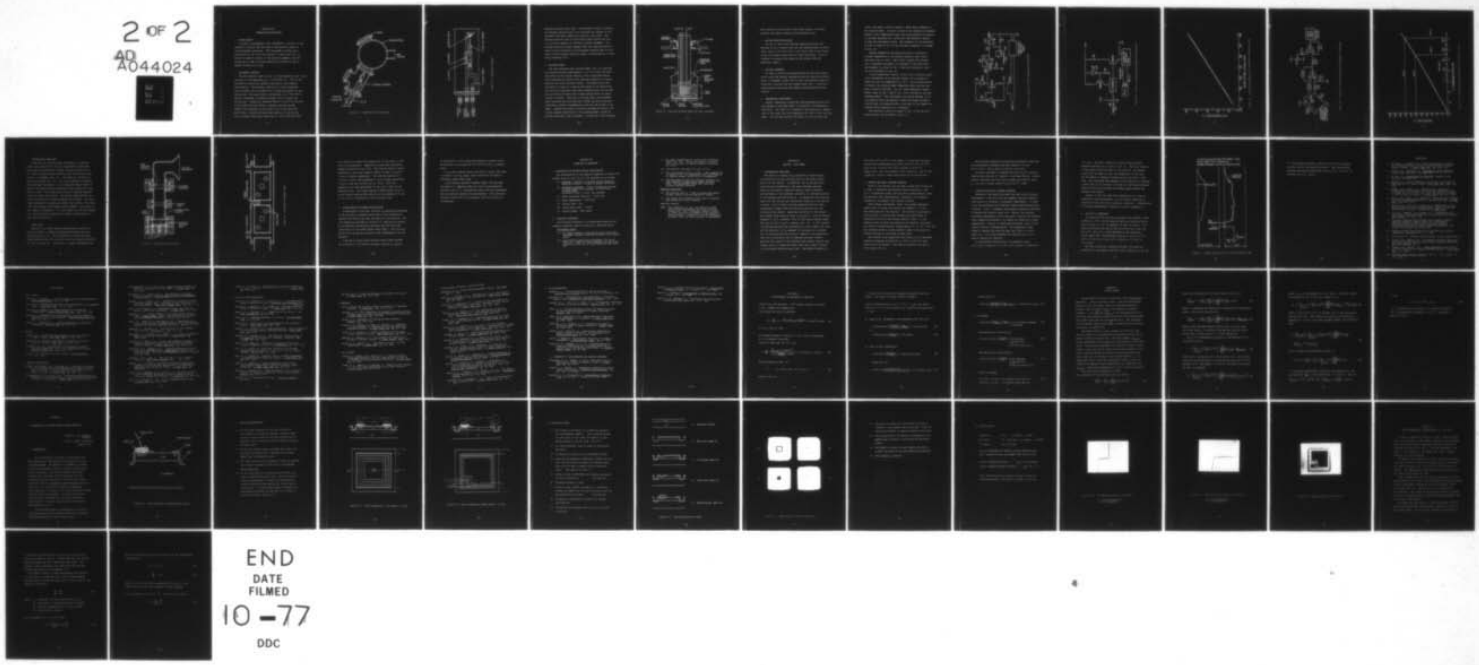
Part Three of the "Chemical Generation of Excited Oxygen" program involved the analysis of the results from the previous phases and subsequent modification of the generator based upon these results. Specifically, this included improving the technique for atomization of the peroxide solution, increasing the width of the cold-band on the rotating dewar, and improving the temperature controllability of the rotating dewar.

After the incorporation of the various modifications into the generator system, numerous runs were carried out. Based on these results, it did not appear to be possible to further increase the $O_2(^1\Delta)/O_2(^3\Sigma)$ yield using Br_2. However, an encouraging preliminary experiment using chlorine in place of bromine lead to an improvement in this yield and thus the ultimate replacement of bromine by chlorine in the final generator configuration.

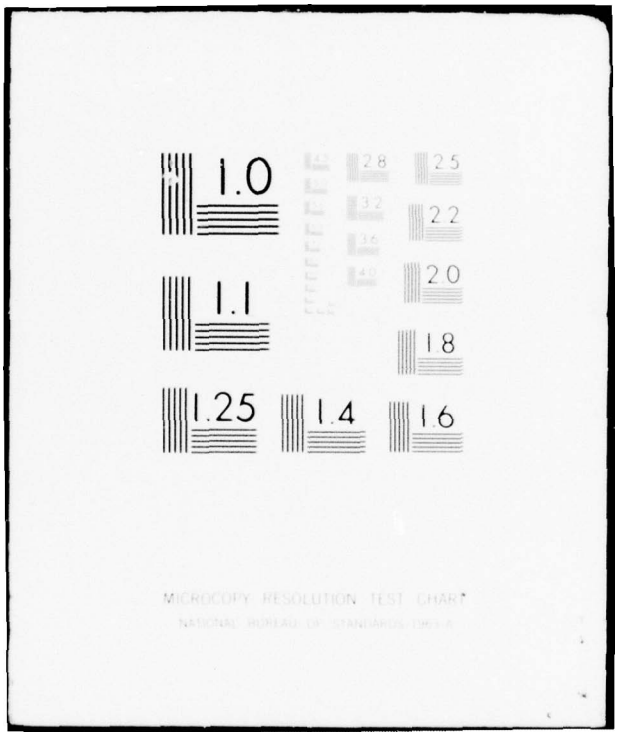
In the final series of tests, the optimum running conditions were determined and the output yield was measured, at which time the chemical generator was delivered to and tested at AFWL.

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CHEMICAL GENERATION OF GASEOUS EXCITED OXYGEN.(U)
AUG 77 P H LEE, W D SLAFER F29601-75-C-0058
UNCLASSIFIED AFWL-TR-76-90 NL

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SECTION XIII

GENERATOR MODIFICATIONS

1. GLASS REACTOR

In order to accommodate a new (hypodermic) atomizer, it was necessary to modify the main body of the reaction vessel to include several side ports. This consisted of adding two 3 glass ports at 120° from the original 2" output arm (Fig. 23). One arm is used to connect to the atomizer assembly, and the second arm is used to provide additional flexibility and is capped off when not in use.

2. HYPODERMIC ATOMIZER

The new atomizer, shown in Fig. 24, was connected to the 3 inch side port of the generator by a 3 inch glass tee. The tee was included to provide for possible variation of the atomizer configuration. The atomizer consists of a solid stainless steel cylinder with a threaded hole through the center for the carrier gas. The input side is fitted with a 1/4 inch tube to which is connected a flexible (nalgene) hose to supply the carrier gas. A specially modified adapter fitting is connected to the output end and allows a standard Luer-Lok syringe needle to be connected to the output side of the stainless steel block. Slightly off-axis and parallel to the carrier hole is another hole which holds the 1/4 inch stainless steel

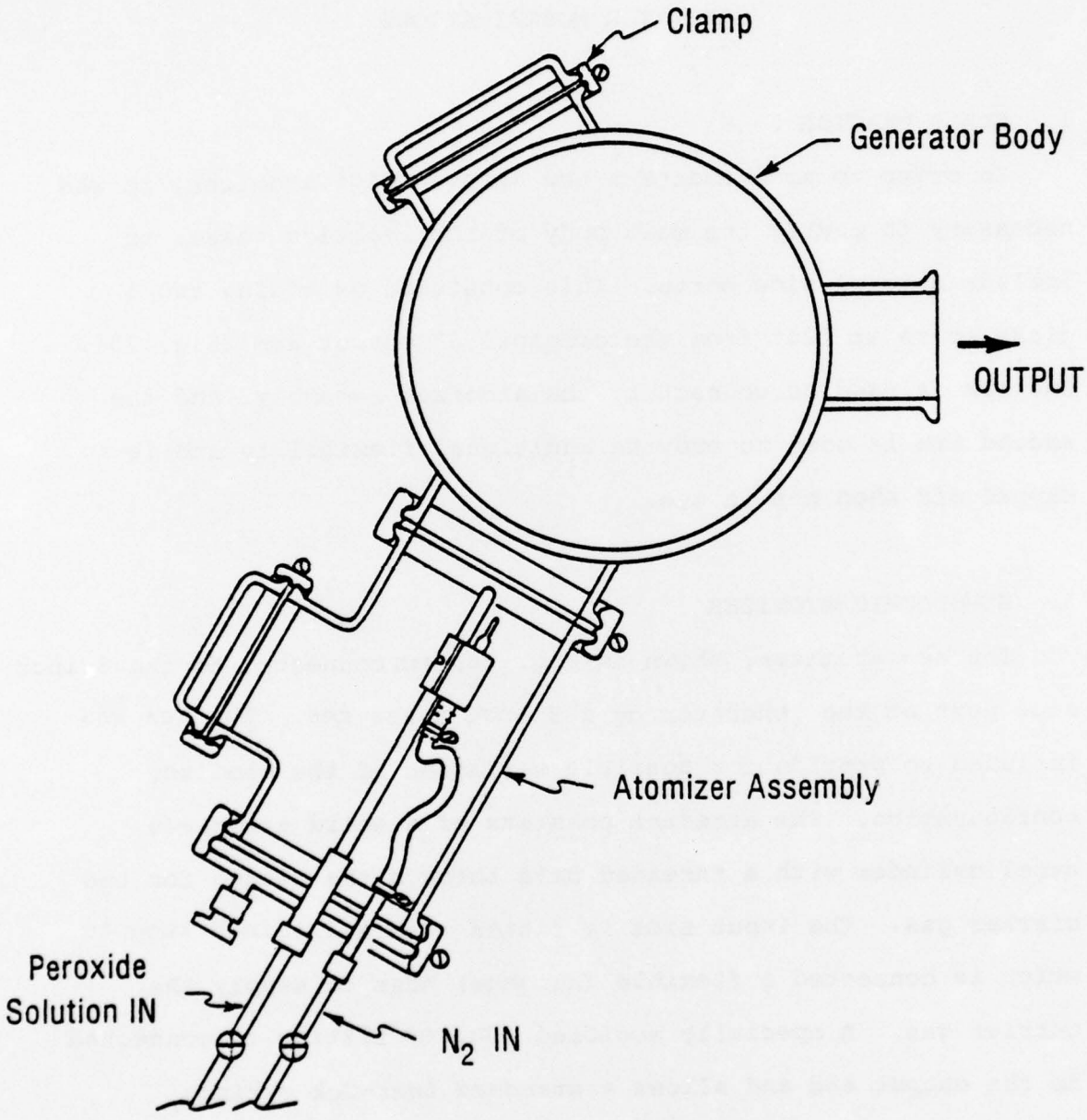


Figure 23. Generator with Side Ports

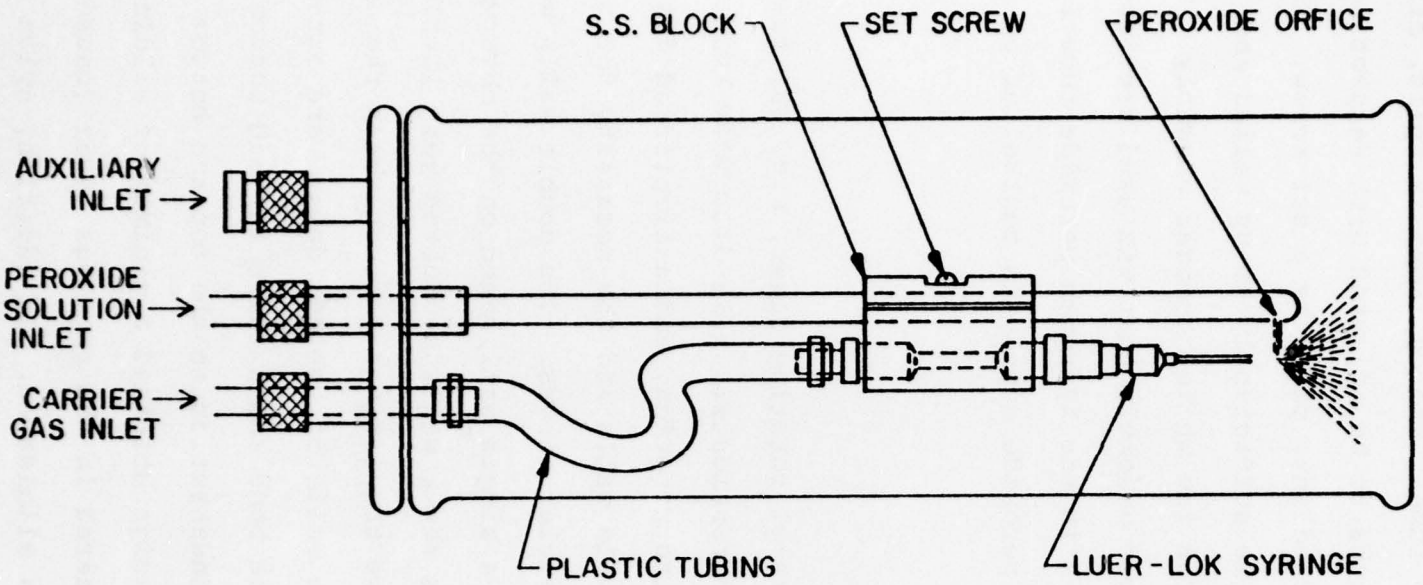


Figure 24. Hypodermic Atomizer

hydrogen peroxide spray tube. The cylinder is split, allowing the hydrogen peroxide tube to be adjusted with respect to the hypodermic and then locked into place by a set screw. The hydrogen peroxide tube is sufficiently heavy walled and long as to provide support for the whole atomizer assembly. The hydrogen peroxide plunger assembly that was used previously to remove orifice blockages in the hydrogen peroxide tube is also used, and the hydrogen peroxide supply is controlled by a glass/Teflon metering valve.

3. ROTATING DEWAR

The new stainless steel rotating dewar, Fig. 25, features the following design improvements: a 1½ inch wide cold band, negligible run-out during rotation, and a simplified design that eliminates the double walls and the necessity for vacuum bake-out and using molecular sieves. The double walls were eliminated in favor of a single wall, based on the observation that the thin stainless steel walls conducted very little heat and thus would not cause the O-rings through which the dewar rotates to freeze. The walls of the new dewar were extended above and below the cold band and a false top and bottom were installed to prevent condensation on the top and bottom of the dewar. Because this design utilized a minimum of welding, the run-out problem encountered in the previous dewar (caused by welding distortion) was eliminated. In addition, nylon bushings

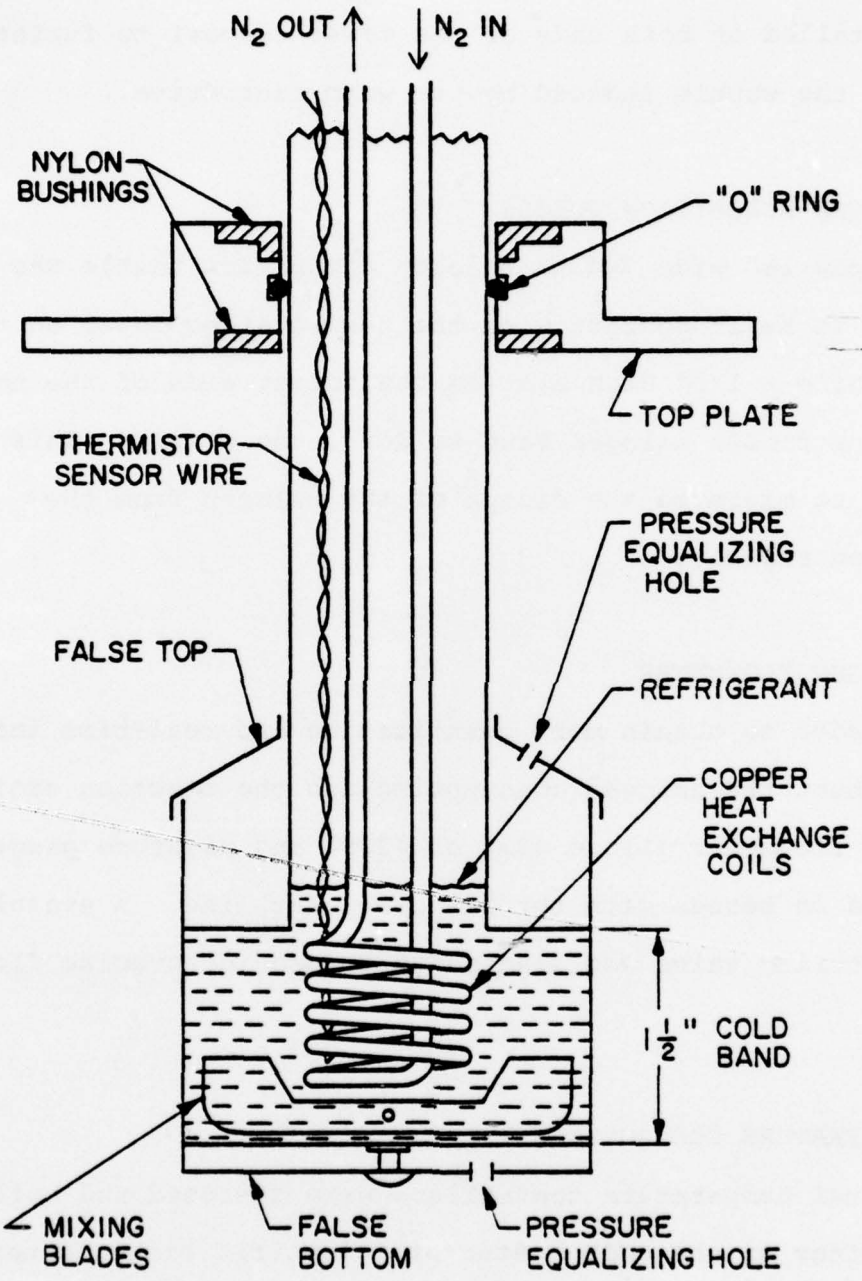


Figure 25. Modified Rotating Dewar and Heat Exchanger

were installed on both ends of the dewar support to further minimize the wobble induced by the worm-gear drive.

4. HALOGEN DEPOSITION NOZZLE

The new 1½" wide Teflon halogen deposition nozzle was designed to be in contact with the new rotating dewar on three sides, while a 1/8" high slot on the output side of the nozzle allows the frozen halogen band to leave the nozzle. This is intended to minimize the escape of the halogen from the deposition region.

5. *HALOGEN FLOWMETER*

In order to obtain more quantitative and real-time information about the halogen consumption and the reaction stoichiometry, a flowmeter (Linde 4334 or 4335) and pressure gauge was installed in series with the halogen inlet line. A stainless steel metering valve was also added to provide precise flow control.

6. TEMPERATURE CONTROLLERS

Several temperature controllers were designed and built by John Deffner of the UCSB Master of Scientific Instrumentation laboratory. The first is a thermostat that maintains a temperature in the range from room temperature to -80°C in the rotating dewar. This device controls the amount of cold nitrogen gas

(from a ℓN_2 dewar) running through a copper heat exchanger in the rotating dewar. Acetone is used as the temperature exchange medium in this temperature range, and mixing blades are mounted on the heat exchange coil (along with the thermistor sensor) to keep the refrigerant mixed. The schematic of the electronic circuit is shown in Fig. 26 and the heat exchanger is included in Fig. 25.

Another temperature controller was built to maintain a constant temperature in the bromine reservoir bath, which typically runs at +40°C. The circuit controls the current into a nichrome resistance coil immersed in the water bath. The schematic is given in Fig. 27 and the calibration curve for the controller in Fig. 28.

A third temperature control circuit uses a platinum resistance thermometer as the sensing element and is capable of operation from ℓN_2 temperature to -30°C. This device was used to control the rotating dewar temperature when chlorine was used in place of bromine. For the lower temperature experiments, Freon 22 (mp = -160°C; bp = -41°C) was used as the heat exchange medium. This refrigerant was chosen because of its low freezing point and because it does not become extremely viscous near its freezing point, as do many of the common low freezing point solvents (e.g., alcohols).

The controller circuit is shown in Fig. 29 and the calibration curve for the device in Fig. 30.

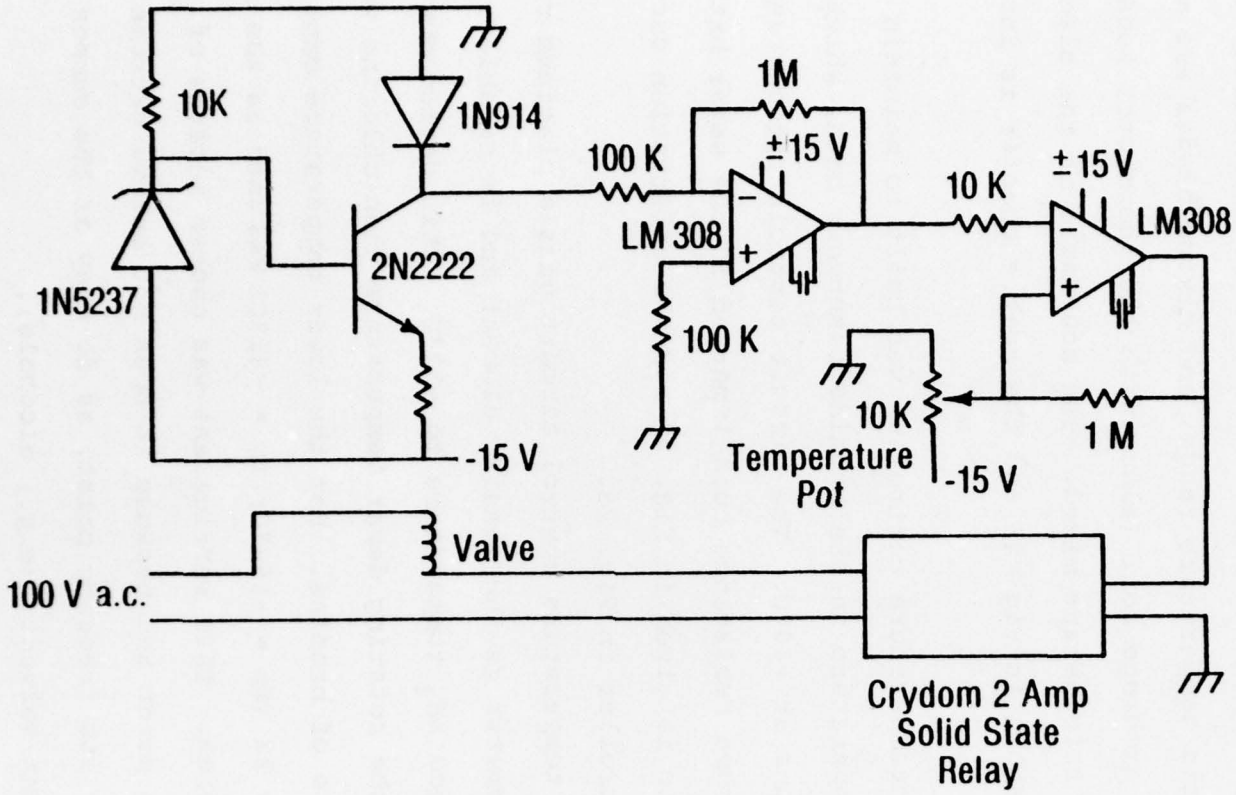


Figure 26. Circuit of -80°C Temperature Controller

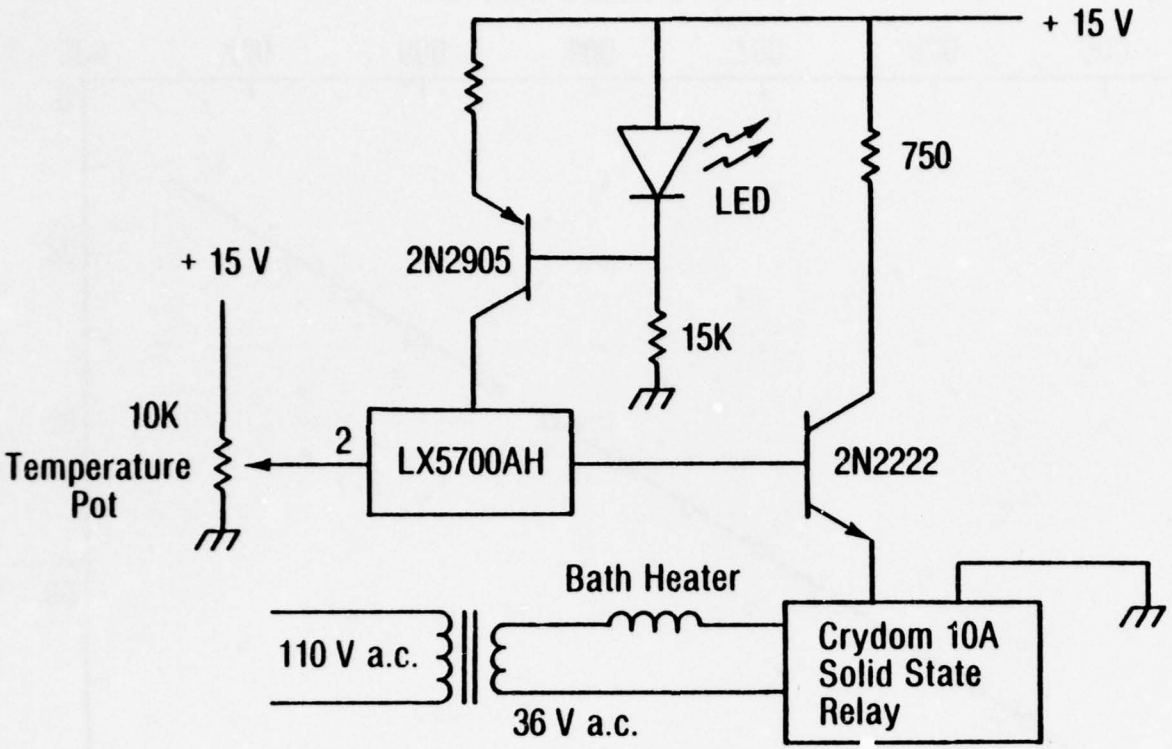


Figure 27. Circuit of Bromine Bath Temperature Controller

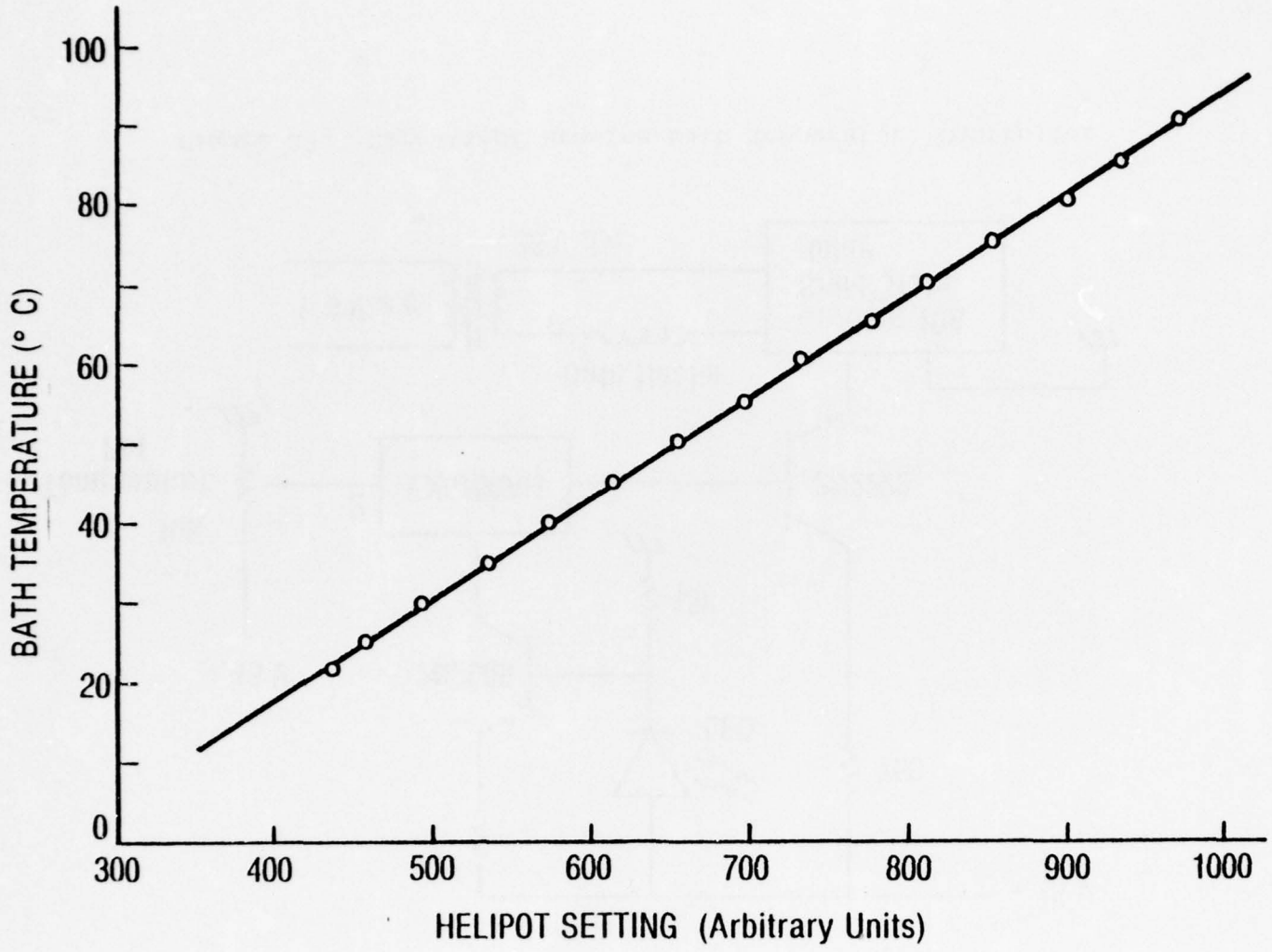


Figure 28. Bromine Bath Temperature Controller Calibration Curve

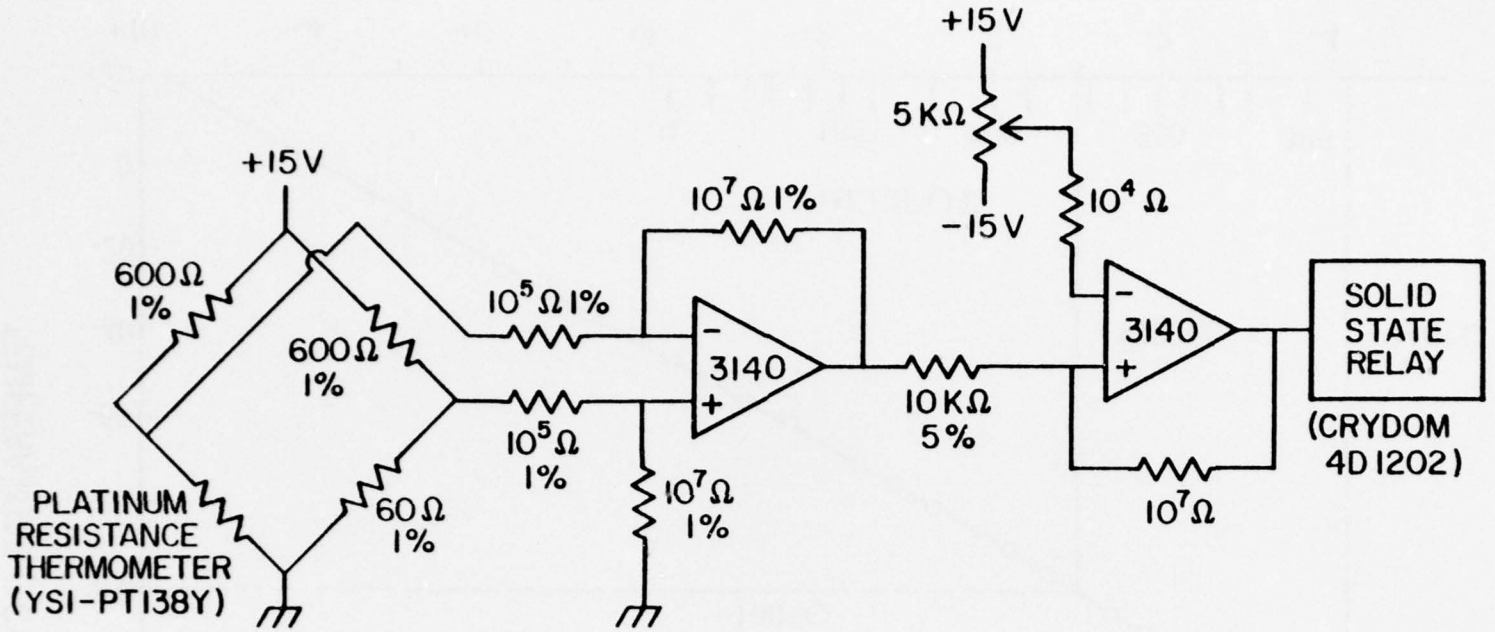


Figure 29. Circuit of Platinum Resistance Thermometer Controller

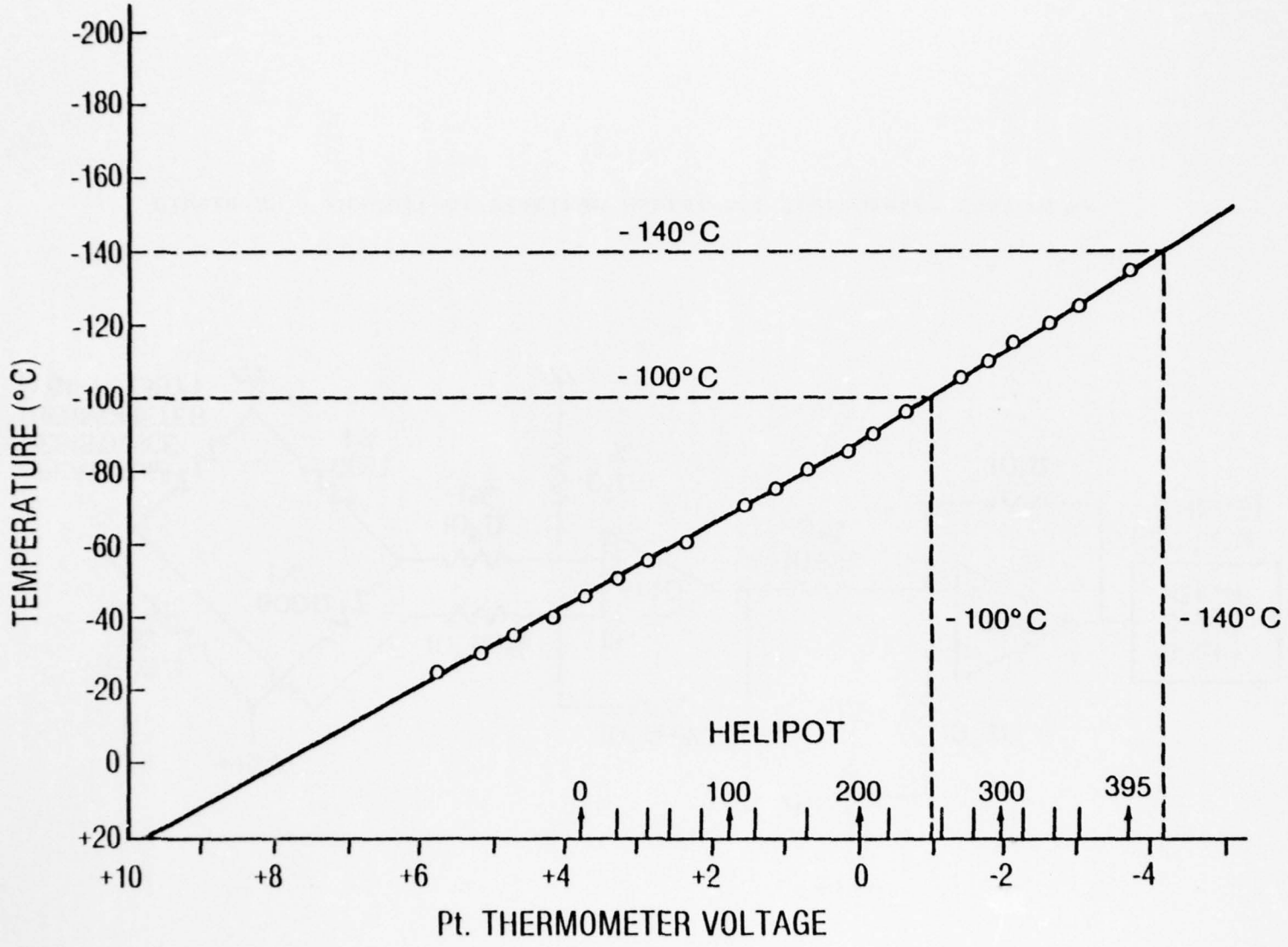


Figure 30. Platinum Resistance Thermometer Calibration Curve

7. PIEZOELECTRIC NEBULIZER

Along with the rotating dewar experiments, a parallel effort was carried out to build a piezoelectric nebulizer, which uses a piezoelectric crystal (barium titanate) drive at ~1 MHz to break up salt solutions into very uniform droplets of ~5μ diameter (Ref. 12). The nebulizer consists of three main stages (Fig. 31). The first contains the crystal, which has been covered by a 1 mil aluminized Teflon sheet to protect the crystal and is connected to the crystal by a very thin oil film. This stage also contains a hydrogen peroxide inlet just above the crystal. The second stage consists of a Teflon ring by which nitrogen sweeper gas is added. The final stage consists of a halogen gas radial ring injector with eight .020 inch diameter holes aimed slightly upward. The output of this stage is connected to a 3 inch sideport of the main generator, and the standard pumping and trapping configuration is used from this point on.

8. OUTPUT TRAP

Because of the lower trapping temperatures required for chlorine removal, a compact ℓN_2-cooled cross-tube trap was constructed (Fig. 32). This consisted of a stainless steel jacket welded around the trap with input and output connections for cold nitrogen gas. In addition, a copper thermometer well

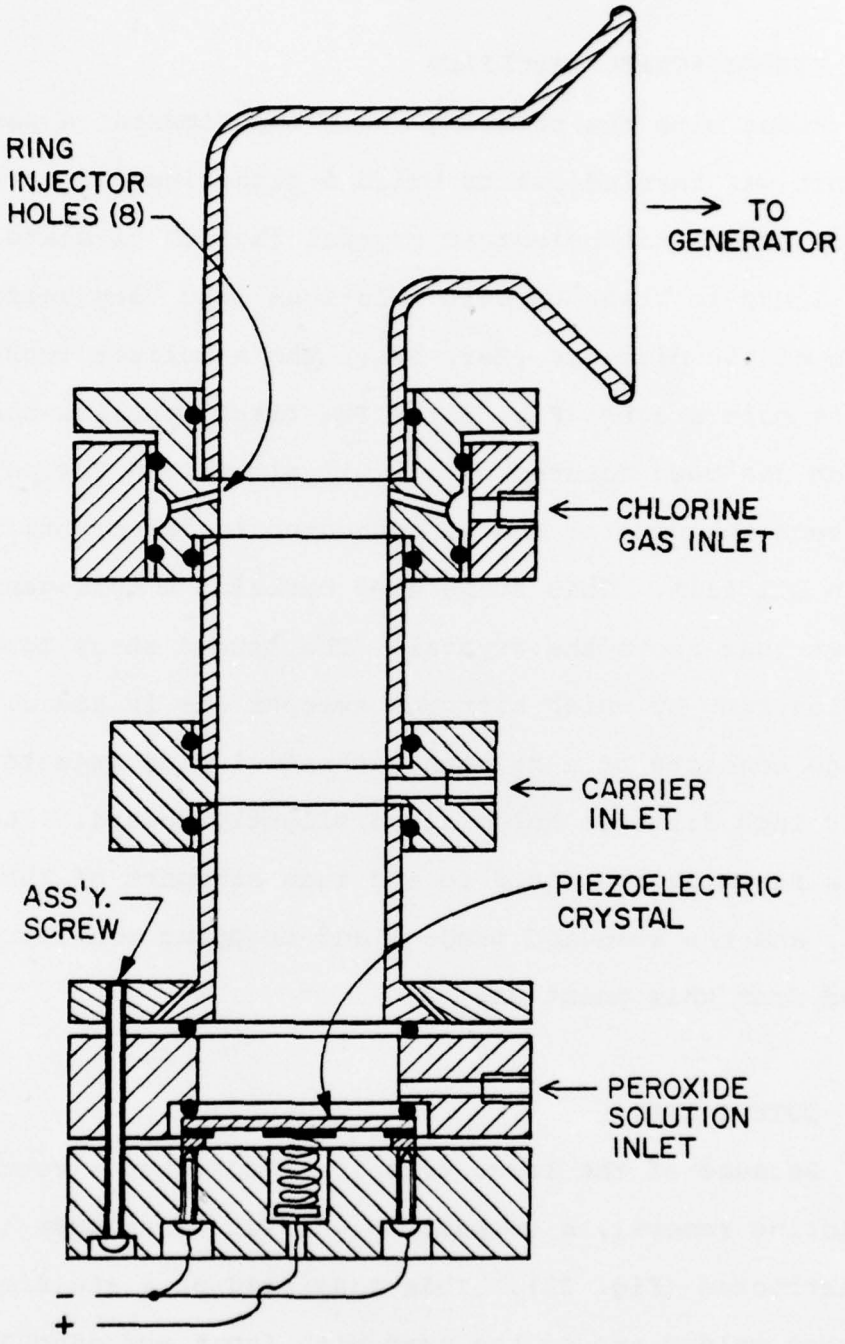


Figure 31. Piezoelectric Nebulizer

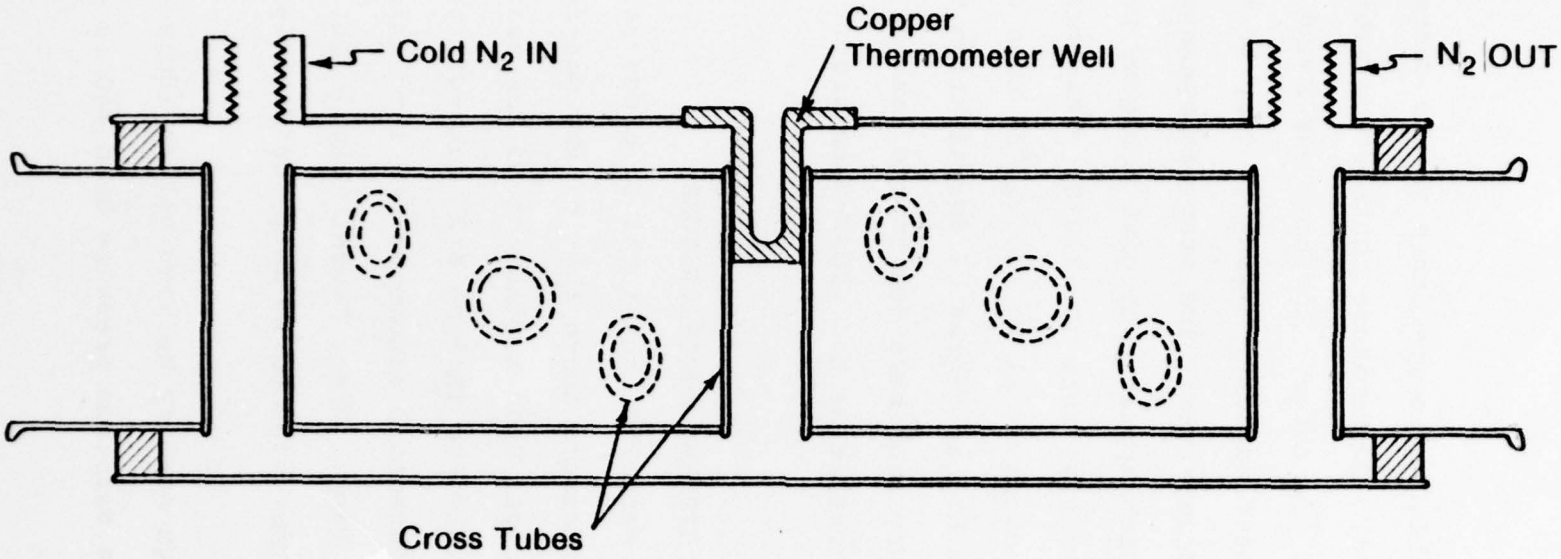


Figure 32. Cross-Tube Cryogenic Trap

was installed to enable the temperature in the center of the trap to be determined. Temperature control was achieved by manually setting the ℓN_2 valve. The trap was found to have a sufficiently large heat capacity making it easy to maintain a fairly constant temperature. The trap was operated at -150°C to -160°C, which appeared to give a higher percentage of $O_2(^1\Delta)$ than did initial runs at ~120°C. This trap appeared to be less detrimental to the $O_2(^1\Delta)$ than did the fast-flow trap. The higher degree of deactivation of $O_2(^1\Delta)$ by the latter trap may have been due to the inability to cool it to as low a temperature as the cross-tube trap.

9. MISCELLANEOUS EQUIPMENT MODIFICATIONS

As mentioned in Part Two, the total O_2 pressure was measured as the increase in pressure above that of the non-reacting reagents and carrier gas upon initiation of the reaction. The flow system was modified to include a 2" take-off arm leading to the Baratron differential manometer and into which was inserted an in-line Perkin Elmer "Versa Trap." This trap was cooled with ℓN_2 and was intended to keep condensables from the Baratron.

A new set of high quality bellows valves (Hoke 4251N6M) was connected to the Baratron pressure head and is capable

of maintaining a high vacuum and preventing leakage across the Baratron, as was required for accurate total O_2 measurements.

A ℓN_2 level sensing device was used to control the level in either of the ℓN_2 traps, thus eliminating the need to constantly check these traps.

A dual channel recorder (Sandborn Model 320) was made available on a temporary basis for use in simultaneously recording the $O_2(^1\Delta)$ fluorescence signal from the picoammeter and the pressure reading from the Baratron. This permitted accurate correlation of the pressure rise with the $O_2(^1\Delta)$ fluorescence.

SECTION XIV

OPERATION OF GENERATOR

1. DESCRIPTION OF OPTIMUM SYSTEM CONFIGURATION

The configuration of the chemical generator for which the highest yield of $O_2(^1\Delta)/O_2(^3\Sigma)$ was produced is as follows:

(1) Reagents: chlorine (~3.0 SLM) and 90% hydrogen peroxide solution, 17% NaOH by weight (45 ml/min).

(2) Hypodermic atomizer: 4 torr nitrogen gas through 16 gauge needle with atomizer ~2 inches from rotating dewar
Peroxide orifice = 0.0135 inch diameter

(3) Dewar rotational velocity: ~15-28 rpm

(4) Dewar temperature: -125°C±5°C

(5) Gravity trap: ℓN_2

(6) Cross-finger trap: ~-155°C

(7) Pumping speed: 1000 cm/sec

2. OPERATION PROCEDURE

The following procedure is followed when operating the chemical generator under the conditions described above:

Preliminary Setup

(a) Set pumping speed to 1000 cm/sec with carrier gas (nitrogen) through calibrated flowmeter and pressure gauge.

(b) Load rotating dewar with refrigerant (275 ml of Freon 22). Dewar and heat exchange coil should be pre-chilled with ℓN_2 to avoid excessive Freon boil-off.

(c) Set dewar thermostate at -130°C (see calibration curve, Fig. 38). During cool-down, it is advisable to run dewar to prevent possible freeze-up of O-ring.

(d) Load gravity trap dewar 2/3 full of ℓN_2.

(e) Cool cross-finger trap to -155°C. When temperature is below -41°C, fill thermometer well with Freon 22 to improve thermal conductivity to thermometer.

(f) Load peroxide solution and evacuate peroxide line from generator to separatory funnel stopcock.
NOTE: Use HALOCARBON grease ONLY with high-strength hydrogen peroxide.

Reaction Initiation

(g) Set chlorine flow to ~3 SLM (a yellow band should be seen leaving chlorine deposition nozzle).

(h) With glass Teflon metering valve open to maximum, open separatory funnel stopcock.

(Reaction begins)

NOTE: Upon completion of run, care should be taken during cleanup procedures as frozen chlorine sublimes at >-101°C and could present a hazard to those involved in handling of the generator during cleanup. Always cool chlorine containing equipment with ℓN_2 before opening to atmosphere.

SECTION XV

RESULTS - PART THREE

1. PIEZOELECTRIC NEBULIZER

The efforts to operate the piezoelectric atomizer were frustrated by continual malfunctioning of the power supply/driver for the crystal. In addition, due to the base catalyzed peroxide decompostion, the basic hydrogen peroxide solution continuously generated numerous large O_2 bubbles when operated at low pressures, resulting in a refluxing action of the hydrogen peroxide solution. By separating the refluxing stage from the carrier gas introduction stage by a long section of glass, a mist of basic hydrogen peroxide solution could nonetheless be swept from the refluxing solution into the chlorine mixing region. Operating the device in this manner gave rather large flows of total O_2 and $O_2(^1\Delta)$, with the partial pressure of $O_2(^1\Delta)$ reaching ~140μ at 1000 cm/sec pumping speed. The yield of $O_2(^1\Delta)/O_2(^3\Sigma)$, however, was 11%. In this reactor the hydrogen peroxide was introduced at a much higher flow rate, and the production of O_2 appeared to increase with increased flow of hydrogen peroxide solution, leading to the speculation that the O_2 production rate is hydrogen peroxide limited. Applying this result to the rotating dewar reactor implies that greater total O_2 yields may result when using larger orifices in the hydrogen peroxide spray tube. The possible effects on

the ratio $O_2(^1\Delta)/O_2(^3\Sigma)$ is not known. To this end, two more nozzles were constructed with 0.020 inch and 0.024 inch diameter holes, giving a flow rate increase of x2 and x3, respectively, over the standard 0.0135 inch hole. Due to time limitation, tests of these tubes could not be carried out.

2. BROMINE AND BASIC HYDROGEN PEROXIDE

Tests of the bromine rotating dewar system were carried out in order to determine the optimum running conditions. The $O_2(^1\Delta)$ fluorescence signal and the total system pressure (from the Baratron) were simultaneously recorded on two separate channels of the Sandborn Dual Channel recorder.

After several preliminary tests, the optimum hypodermic needle size (16 guage) and carrier gas pressure (~4 torr) were determined for the atomizer. This device now produced a uniform spray of droplets and achieved the best degree of atomization of any of the nozzles tested to date. In the pressure range at which the generator was operated, the spray was found to diverge rapidly (approximately 90° to 120° cone) and was therefore moved to within several inches of the drum for optimum coverage of the frozen halogen band.

The rotating drum temperature was found to be an important operating parameter and was set at -55°C to -60°C for best results with the bromine. The bromine reservoir was kept at +40°C during the run.

The optimized generator configuration produced a yield for the bromine/basic hydrogen peroxide system of ~16% for $O_2(^1\Delta)/O_2(^3\Sigma)$, with a total O_2 flow of ~0.25 torr.

An effort was made to increase the $O_2(^1\Delta)/O_2(^3\Sigma)$ ratio by substituting chlorine for bromine in the above system. Initial results indicated that this gave a higher net yield of total O_2 (~x2) and a higher yield of $O_2(^1\Delta)/O_2(^3\Sigma)$ (>20%).

3. CHLORINE AND BASIC HYDROGEN PEROXIDE

Because of the results obtained from the initial chlorine experiments, it was felt that the emphasis should be shifted from bromine to chlorine in subsequent experiments. In order to run the generator with chlorine, several modifications were required. First, a flowmeter and pressure gauge were installed to measure the chlorine input flow. Second, the platinum resistance thermometer circuit was used to control the rotating dewar temperature because it is capable of operating at lower temperatures. Finally, as mentioned previously, Freon 22 was used as the heat exchange medium. The temperature range chosen to operate the rotating dewar was -120°C to -130°C, which gave a low vapor pressure for chlorine but did not seem to inhibit the reaction.

In the optimum configuration, the generator gave a $O_2(^1\Delta)/O_2(^3\Sigma)$ yield of 20 to 24%, with a total O_2 pressure of

~0.5 torr. The chart record of a typical chlorine-basic hydrogen peroxide run is given in Fig. 33. The major impurity in the output stream was found to be chlorine. The amount varied with the type of trap, the temperature of the trap, and the amount of material already coating the walls of the trap. The cross-tube trap appeared to be efficient at removing a great deal of the chlorine, but even at -160°C some chlorine passed through the trap when the pumping speed reached and exceeded 1000 cm/sec.

Several of the runs were batch sampled and the total O_2 measured by mass spectrometer, and the results essentially agreed with the real-time O_2 measuring technique. A description of the mass spectrometric analysis is given in Appendix D.

4. DELIVERY OF GENERATOR

The generator and ancillary equipment were shipped to AFWL on March 16, 1977, and the Quantum Institute group arrived at AFWL on March 21, 1977,to assemble and test the device. The chemical generator was set-up and run during this time, and the $O_2(^1\Delta)$ and $O_2(^3\Sigma)$ yields measured by EPR techniques. During these runs, the generator produced a yield of $O_2(^1\Delta)/O_2(^3\Sigma)$ of 19% with a total $O_2(^3\Sigma)$ output of ~0.5 torr at ~700 cm/sec.

The only significant difference between the operating conditions at the Quantum Institute and at AFWL was in the use

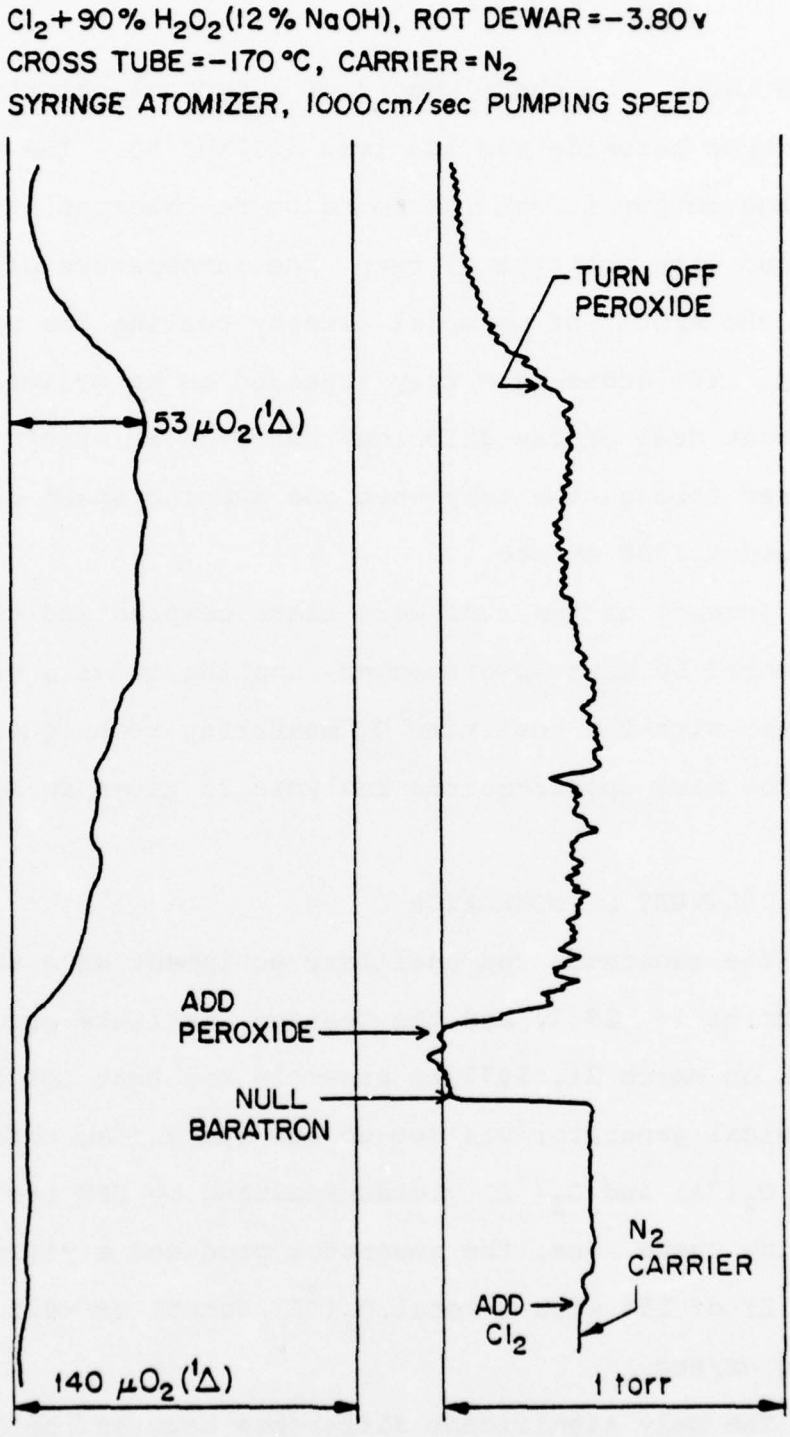


Figure 33. Sample Chart Record of Chlorine-Peroxide Run

of ~75% hydrogen peroxide at AFWL in place of 90% hydrogen peroxide used at the Quantum Institute. Less concentrated hydrogen peroxide has been shown (Section XI.3, Part Two) to decrease the $O_2(^1\Delta)$ yield.

REFERENCES

1. Kajiwara, T., Kearns, D.R., "Direct Spectroscopic Evidence for a Deuterium Solvent Effect on the Lifetime of Singlet Oxygen in Water," J. Amer. Chem. Soc., 95, 5886, 1973.

2. Cotton, F.A., Wilkinson, G., Advanced Inorganic Chemistry, Interscience, New York, 1966, pag. 570.

3. Jolles, A.E., Bromine and its Compounds, Academic Press, New York, 1966, pg. 156.

4. Kaufman, F., "The Air Afterglow and its use in the Study of Some Reactions of Atomic Oxygen," Proc. Roy. Soc., A247, 123, 1958.

5. Badger, R.M., Wright, A.C., Whitlock, R.F., "Absolute Intensities of the Discrete and Continuous Absorption Bands of Oxygen Gas at 1.26 and 1.065 N and the Radiative Lifetime of the $^1\Delta_g$ State of Oxygen," J. Chem. Phys., 43, 4345, 1965.

6. Golde, M.F., Roche, A.E., Kaufman, F., "Absolute Rate Constant for the O+NO Chemiluminescence in the Near Infrared," J. Chem. Phys., 59, 3953, 1973.

7. Woolsey, G.A., Lee, P.H., Slafer, W.D., "Measurement of the Rate Constant for NO-O Chemiluminescence Using a Calibrated Piston Source of Light," accepted by J. Chem. Phys.

8. Lee, P.H., Woolsey, G.A., Slafer, W.D., "Integration Over Cylindrical Luminous Volumes Using a Calibrated Piston Source," Appl. Optics, 15, 2825, 1976.

9. The solid chemicals were obtained from Monsanto Inorganic Chemicals Division, Newport Beach, CA. The Monsanto catalogue numbers are ACl-59 for potassium dichloro-isocyanurate, ACl-60 for sodium dichloroisocyanurate, and ACl-66 for the penta-s-triazine salt.

10. "Chemical Safety Data Sheet SD-53," Manufacturing Chemists Association, Washington, D.C., 7, 1969.

11. Pilipovitch, D., Rockwell Science Center, Private Communication.

12. Denton, M.B., Swartz, D.B., "An Improved Ultrasonic Nebulizer System for the Generation of High Density Aerosol Dispersions," Rev. Sci. Instrum., 45, 81.

13. Browne, R.F., Ogryzlo, E.A., "Chemiluminescence from the Reaction of Chlorine with Aqueous Hydrogen Peroxide," Proc. Chem. Soc., 117, 1964.

14. Chemical Rubber Company Handbook, 49th Ed., Chem. Rubber, Co., F151, 1968.

BIBLIOGRAPHY

1. EARLY PAPERS

Gattow, G., Schneider, A. "Eine Anorganistche Lumineszenzreaktion", Naturwissenschafter, 41, 116, 1954 .

Groh, M.P., "Présentation de Réactions Accompagnées de Luminescence Rouge:, Bull. Soc. Chim., 5, 12, 1938 .

Groh, M.P., Kirrmann, A, "Étude Spectrale d'une Réaction Luminescente", Comptes Rendus Acad. Sci., 215, 275, 1942 .

Mallet, L., "Phénoménes de Luminescence au Cours de Réactions Oxydantes en Solutions Aqueuses", Comptes Rendus Acad. Sci, 185, 352 (1927).

Stauff, J., Schmidkunz, H., "Chemilumineszenz von Oxydations-reaktionen", Z. Phys. Chem, 34, 295, 1962 .

2. REVIEWS

Foote, C.S., "Photosensitized Oxygenations and the Role of Singlet Oxygen", Acc. Chem. Res. 1, 104, 1968 .

Kearns, D.R., "Physical and Chemical Properties of Singlet Molecular Oxygen", Chem. Rev., 71, 395, 1971 .

Trozzolo, A.M. ed, "International Conferences on Singlet Molecular Oxygen and its Role in Environmental Science", Ann. N.Y. Acad. Sci., 171, 1-302, 1970 .

Wayne, R. P., "Singlet Molecular Oxygen", Adv. Photochem., 7, 311, 1969 .

3. GENERAL SPECTROSCOPY

Badger, R.M. Wright, A.C., Whitlock, R.F., "Absolute Intensities of the Discrete and Continuous Absorption Bands of Oxygen Gas at 1.26 and 1.065μ and Radiative Lifetime of the $^1\Delta_g$ State of Oxygen", J. Chem. Phys, 43, 4345, 1965 .

Blickensderfer, R.P., Ewing, G.E., "Collision-Induced Absorption Spectrum of Gaseous Oxygen at Low Temperatures and Pressures. I. The $^1\Delta_g - ^3\Sigma_g$-System", J.Chem. Phys., 51, 873, 1969 .

Blickensderfer, R.P., Ewing, G.E., "Spectroscopic Evidence for Binary O_2 Clusters in the Gas Phase", J. Chem. Phys, 47, 331 , 1967 .

Davidson, J. A., Ogryzlo, E. A., "The Quenching of Singlet Molecular Oxygen," Chemiluminescence and Bioluminescence, Plenum Press, N.Y., p. 111, 1973

Derwent, R. G., Thrush, B. A., "Excitation of Iodine by Singlet Molecular Oxygen, Part 2, Kinetics of the Excitation of the Iodine Atoms," Chem. Soc. Faraday Disc.. 53, 162, 1972.

Foner, S.N., Hudson, R.L., "Metastable Oxygen Molecules Produced by Electrical Discharges", J. Chem. Phys, 601 , 1956 .

Franklin, R. D., "Kinetic Model of the Oxygen-Iodine Transfer Laser," Laser Digest, Summer, 1974, AFWL-TR-74-241, p.280, Air Force Weapons Laboratory, Kirtland AFB, NM, 1974 .

Gann, R.G., Bogan, D.J., Frankiewicz, T.C., "Determination of $O_2(^1\Delta)$ from 300-900°K", paper given at "The First Chemical Congress of the North American Continent", paper #175, 1975 .

Herzberg, L., Herzberg, G., "Fine Structure of the Infrared Oxygen Bands", Astrophys. J., 105, 353, 1947.

Katayama, D.H., Huffman, R.E., Tanaka, Y., " $O_2(a^1\Delta_g)$ Absorption Bands in the Vacuum Ultraviolet", J.Chem. Phys., 62, 2929 (1975).

Kajiwara, T., Kearns, D.R., "Direct Spectroscopic Evidence for a Deuterium Solvent Effect on the Lifetime of Singlet Oxygen in Water", J. Amer. Chem. Soc., 95, 5886 , 1973 .

MacKnight, A.D., Modreski, P.J., "Chemical Generation of Electronically Excited Oxygen", Laser Digest, Spring 1974, AFWL-TR-74-100, 319, Air Force Weapons Laboratory, Kirtland AFB, NM, 1974.

Matheson, I.B.C., Lee, J., "The Lifetime of $(^1\Delta_g)$ Oxygen in Solution," Chem. Phys. Letters., 14, 350, 1972 .

Parker, J.G., "A Study of the Role of Vibration-Vibration Exchange on the Collisional Deactivation of Vibrationally Excited Singlet Molecular Oxygen", J. Chem. Phys, 61, 3408,1974.

Steer, R.P., Ackerman, R. A., Pitts, J. N., "Singlet Oxygen in the Environmental Sciences V. Rates of Deactivation of $O_2(^1\Delta_g)$ by Oxygen and Nitrogen," J. Chem Phys. 51, 843, 1969.

Tsai, S.C., Robinson , G. W., "Why is Condensed Oxygen Blue?", J. Chem. Phys, 51, 3559, 1969.

Young, R. A., Black, G., "Measurement of the Rate Coefficient of $O_2(a^1\Delta) + O_2(a^1\Delta) \rightarrow O_2\ (b^1\Sigma) + O_2\ (X^3\Sigma)$," J. Chem. Phys, 42, 3740,1965.

4. SOLUTION CHEMILUMINESCENCE

Arnold, J. S., Browne, R. J., Ogryzlo, E. A., "The Red Emission Bands of Molecular Oxygen," Photochem. and Photobiol, 4, 963,1965.

Arnold, S.J., Ogryzlo , E. A., Witzke, M., " Some New Emission Bands of Molecular Oxygen," J. Chem. Phys, 40, 1769, 1964.

Bader, L. W., Ogryzlo, E. A., "Reactions of $O_2(^1\Delta g) + O_2\ (^1\Sigma g^+)$, Disc. Faraday Soc, 37, 46, 1964.

Bowen, E. J., "Chemiluminescence in Solution," Pure and Appl. Chem, 9, 473,1964.

Bowen, E. J., Lloyd, R. A., Chemiluminescence from Dissolved Oxygen," Proc. Chem. Soc, 305, 1963.

Browne, R. J. Ogryzlo, E. A., Chemiluminescence from the Reaction of Chlorine with Aqueous Hydrogen Peroxide," Proc. Chem. Soc, 117, 1964.

Browne, R. J. Ogryzlo, E. A., "The Yield of Singlet Oxygen in the Reaction of Chlorine with Hydrogen Peroxide," Can. J. Chem, 43, 2915, 1965.

Khan, A. U., Kasha, M., "Red Chemiluminescence of Molecular Oxygen in Aqueous Solutions," J. Chem Phys, 39, 2105, 1963.

Khan, A. U., Kasha, M. "Rotational Structure in the Chemiluminescence in Spectrum of Molecular Oxygen in Aqueous Systems," Nature, 204, 241, 1964.

Khan, A. U., Kasha, M., "Physical Theory of Chemiluminescence in Systems Evolving Molecular Oxygen," J. Amer.Chem. Soc, 88, 1574, 1966.

Khan, A. U., Kasha, M., "Chemiluminescence Arising From Simultaneous Transitions of Pairs of Singlet Oxygen Molecules," J. Amer. Chem. Soc.,92, 3293,1970.

McKeown, E., Waters, W.A., Chemiluminescence as a Diagnostic Feature of Heterolytic Reactions Which Produce Oxygen," Nature, 203, 1063, 1964.

Seliger, H. H.,"Photoelectric Method...",Analyt. Biochem, 1, 60,1960.

Seliger, H. H. , "Chemiluminescence of H_2O_2-NaOCl Solutions," J. Chem. Phys, 40, 3153, 1964.

5. CHEMISTRY

Cahill, Taube "Use of Heavy Oxygen in Reactions of Hydrogen Peroxide," J. Chem. Soc., 74, 2312, 1952.

Connick, R. E., "The Interaction of Hydrogen Peroxide and Hypochlorous Acid in Acidic Solutions Containing Chloride Ion," J. Amer. Chem. Soc, 69, 1509 1947.

Foote, C. S., "Mechanism of Photosensitized Oxidation," Science, 162, 963, 1968.

Foote, C. S., Wexler, S., Ando, W., Higgins, R., "Chemistry of Singlet Oxygen. IV Oxygenations with Hypochlorite-Hydrogen Peroxide," J. Amer. Chem. Soc, 90, 975, 1968.

Foote, C. S., Wexler, S., "Olefin Oxidations with Excited Singlet Molecular Oxygen," Amer. Chem. Soc, 86, 3879, 1963.

McKeown, E., Waters, W. A., "The Oxidation of Organic Compounds by 'Singlet' Oxygen," J. Chem. Soc(B), 1040, 1966.

Winer, A. M., Bayes, D. D., "The Decay of $O_2(a^1\Delta)$ in Flow Experiments," J. Chem. Phys, 70, 302, 1966.

6. NO-O SYSTEM

Fontijn, A., Meyer, C.B., Schiff, M. I., "Absolute Quantum Field Measurements of the NO-O Reaction and Its Use as a Standard for Chemiluminescent Reactions", J. Chem. Phys, 40, 64, 1964.

Golde, M. F., Roche, A. E. Kaufman, F., "Absolute Rate Constant for the O+NO Chemiluminescence in the Near Infrared," J. Chem. Phys, 59, 3953, 1973.

7. MISCELLANEOUS SOURCES OF EXCITED OXYGEN

Chandross, E. A., "A New Chemiluminescent System," Tet. Lett, 12, 761, 1963.

Cook, T. J., Miller, T. A., "Production of $^1\Delta g$ 02 from Micro-wave Discharges in CO_2, NO_2 and SO_2," Chem. Phys. Letters 25, 396, 1974.

Corey, E. J., Taylor, W. C., "A Study of the Peroxidation of Organic Compounds by Externally Generated Singlet Oxygen Molecules," J. Amer. Chem. Soc., 86, 3881, 1964.

Jones, I. T. N., Wayne, R. P., "The Photolysis of Ozone by Ultraviolet Radiation V. Photochemical Formation of O_2 ($^1\Delta_g$)," Proc. Roy. Soc. Lond. A, 321, 409, 1971.

Murray, R. W., Kaplan, M. L., "Gas-Phase Reactions of Singlet Oxygen from a Chemical Source," J. Amer. Chem. Soc, 90, 4161, 1968.

Murray, R. W., Lumma, W. C., Jr., Lin, J. W. P., "Singlet Oxygen Sources in Ozone Chemistry: Decomposition of Oxygen-Rich Intermediates," J. Amer. Chem. Soc., 92, 3205, 1970.

Olmsted, J., Karal, G., "Iodine-Sensitized Photoformation of Singlet Oxygen," J. Amer. Chem. Soc, 94, 3305, 1972.

Peters, E. W., Bekowies, P. J., Winer, A. M., Pitts, J. N., "An Investigation of Potassium Perchromate as a Source of Singlet Oxygen," J. Amer. Chem. Soc, 97, 3299, 1975.

Peters, J. W., Pitts, J. M., Rosental , I., Fuhr, M., "A New and Unique Chemical Source of Singlet Molecular Oxygen. Potassium Perchromate," J. Amer. Chem. Soc, 94, 4348, 1972.

Stauff, J., Sander, U., Jaeschke, W., "Chemiluminescence of Perhydroxyl and Carbonate-Radicals," Chemiluminescence and Bioluminescence, Plenum Press, N.Y., 131.

Stauff, J., Huster, H. J., Lohmann, F., Schmidkunz, H., "Chemiluminescence of Oxidation Reactions. V. E.S.R. and the Chemiluminescence of O_2H and OH," (Ger.), Z. Pysik. Chem. (Frankfurt), 40, 64, 1964.

Steer, R. P. , Darnell, K. R., Pitts, J. N., Jr., "The Base-Induced Decomposition of Peroxacetylnitrate," Tetrahedron Letters, No. 43, p. 3765, 1969.

Wasserman, H. H., Scheffer, J. R., "Singlet Oxygen Reactions from Photoperoxides," J. Amer. Chem. Soc., 89, 3073, 1967.

8. ELECTROCHEMISTRY

Benard, D. J., "Electrochemistry of Gallium Arsenide", University of Illinois, Thesis for Ph.D. in Physics, 1972.

Gerishcer, H., "Semiconductor Electrochemistry," UCRL-18145 Preprint from Advances in High Temp. Chemistry, 1961, 1968.

Johnson, E. L., Pool, K. H., Hamm, R. E., "Polarographic Reduction of Oxygen in Dimethylsulfoxide," Analyt. Chem. 38, 183, 1966.

Khan, A. U., "Singlet Molecular Oxygen for Superoxide Anion and Sensitized Fluorescence of Organic Molecules," Science, 168, 476, 1970.

Legg, K. D., Hercules, D. M., "Electrochemically Generated Chemiluminescence of Lucigenin," J. Amer. Chem. Soc., 91, 1902, 1969.

Mauricle, D. L., Hodgson, W. G., "Reduction of Oxygen to Superoxide Anion in Aprotic Solvents," Analyt. Chem., 37, 1562, 1965.

Peover, M. E., White, B. S., "Electrolytic Reduction of Oxygen in Aprotic Solvents: The Superoxide Ion," Electrochimica Acta, 11, 1061, 1966.

Rallo, L. Rampazzo, "Polarographic Reduction of Oxygen in Formamide," J. Electroanalyt. Chem., 16, 61, 1968.

Sawyer, D. T., Roberts, J. L., Jr., "Electrochemistry of Oxygen and Superoxide Ion in Dimethylsulfoxide at Platinum, Gold, and Mercury Electrodes," J. Electroanalyt. Chem., 12, 90, 1966.

9. CHEMISTRY OF ISOCYANURATES AND RELATED COMPOUNDS

Chattaway, F. D., Wadmore, J. Mello, "The Constitution of Hydrocyanic, Cyanic and Cyanuric Acids," J. Chem. Soc., 80, 200, 1902.

Hoste, P. L., Bouret, J., "Bleaching of Textiles by Chloro-organic Derivatives," Industrie Chemique Belge., 32, 360, 1967 (in French).

Mesiah, R. N., "Triazinetriol," Encyclopedia of Chemical Tech., 20, 2nd Ed., J. Wiley, N.Y., 662, 1969.

Robson, H. L., "Hypochlorites and Chloramines," Encyclopedia of Chelmical Tech., 3, J. Wiley, N.Y., 555, 1963.

Smith, E., "Hydantoin," Encyclopedia of Chemical Tech., 11, J. Wiley, N.Y., 141, 1963.

Smolin, E. M., Rapoport, L., "S-Triazines and Derivatives," Intersicence Publishers Inc., N.Y., 1959.

APPENDIX A

STOICHIOMETRY OF HALOGEN/H_2O_2 REACTION

Oxygen flow rate required: 2×10^3 cm/sec through 5 cm tube @ 1 torr (assume room temperature).

The volume flow rate is therefore:

$$60 \times \frac{\pi d^2}{4} \times V = \frac{60 \times 25 \times \pi \times 2 \times 10^3}{4} = 2.36 \times 10^6 \text{ cc/min} \qquad (A1)$$

or 39.4 l/sec @ 1 torr.

At standard pressure (using $P_1V_1 = P_2V_2$) this is equivalent to 3.21 standard liters/min.

Using the ideal gas law, $PV = nRT$,

$$n = \frac{PV}{RT} = \frac{\frac{1}{760} \text{ atm} \times 2.36 \times 10^6 \text{ cc}}{82.06 \frac{\text{cc-atm}}{^\circ\text{K-mole}} \times 295^\circ\text{K}} = 0.128 \text{ moles } O_2 \text{ gas/min} \qquad (A2)$$

From the equation (Ref. 13):

$$X_2 + HO_2^- + OH^- \rightarrow 2X^- + H_2O + O_2 \qquad (A3)$$

where X = Br, Cl

it is seen that the moles of halogen and peroxide used are equal to the moles of oxygen and water formed.

From the required ratio of $O_2(^1\Delta)/O_2(^3\Sigma)$ = 20%, the output flow of $O_2(^1\Delta)$ is 0.021 moles/min or 5.2×10^{15} molecules/cc-sec @ 1 torr.

A. Rate of Br_2 Consumption (from equations (A2) and (A3)):

$$0.128 \text{ moles } Br_2 \left(\frac{159.81 g}{1 \text{ mole}}\right)\left(\frac{1 \text{ ml}}{2.928 g}\right) = 6.9 \text{ ml } Br_2/\text{min} \qquad \text{(A4)}$$

or

$$0.128 \text{ moles } Cl_2 \left(\frac{22.4 \text{ l}}{1 \text{ mole}}\right) = 2.87 \text{ SLM } Cl_2 \qquad \text{(A5)}$$

B. Rate of H_2O_2 Consumption:

$$0.128 \text{ moles } \left(\frac{34 g \ H_2O_2}{1 \text{ mole}}\right) = 4.35 g \text{ pure } H_2O_2/\text{min} \qquad \text{(A6)}$$

Using 30% H_2O_2:

$$4.35 g \ H_2O_2 \left(\frac{1 g \text{ sol'n}}{0.3 g \text{ pure}}\right)\left(\frac{1 \text{ ml}}{1.11 g \text{ sol'n}}\right) = 13 \text{ ml } 30\% H_2O_2/\text{min} \qquad \text{(A7)}$$

Using 90% H_2O_2:

$$4.35g\ H_2O_2\left(\frac{1g\ sol'n}{.90g\ pure}\right)\left(\frac{1\ ml}{1.39g\ sol'n}\right) = 3.48ml\ 90\%\ H_2O_2/min \quad (A8)$$

C. H_2O Formed:

$$0.128\ moles\left(\frac{18g}{1\ mole}\right)\left(\frac{1\ ml}{1g}\right) = 2.3\ ml\ H_2O/min\ produced\ by\ reaction \quad (A9)$$

Non-reacting H_2O from 30% H_2O:

$$13.0\ ml\ 30\%\ sol'n\left(\frac{1.11g}{1\ ml}\right) = 14.4g\ solution \quad (A10)$$
$$-\ 4.4g\ pure\ H_2O_2$$
$$10.0g\ non\text{-}reacting\ H_2O$$

Non-reacting H_2O from 90% H_2O_2:

$$3.48\ ml\ 90\%\ sol'n\left(\frac{1.39g}{1\ ml}\right) = 4.84g\ solution \quad (A11)$$
$$-4.35g\ pure\ H_2O_2$$
$$0.49g\ non\text{-}reacting\ H_2O$$

Total H_2O formed:

$$(10.0\ ml + 2.3\ ml) = 12.3\ ml/min\ using\ 30\%\ H_2O_2 \quad (A12)$$
$$(0.49\ ml + 2.3\ ml) = 2.8\ ml/min\ using\ 90\%\ H_2O_2$$

APPENDIX B
PISTON SOURCE

One proceeds as follows in measuring $O_2(^1\Delta)$ fluorescence absolutely using the piston source: With the spectrometer tuned to 1.27μ, the piston source is calibrated against a standard lamp (an Electro-Optic L-101 Spectral Irradiance Standard). Let i_{std}^{100} and i_{piston}^{100} be the photomultiplier currents when the standard sources and piston source, respectively, are placed 100cm from the spectrometer slit. The irradiance of the standard lamp at 40cm (I_{std}^{40}) is known from its calibration chart, in $\mu W/cm^2/10$ Å.

The piston source is then inserted into the flow tube and the current in the photomultiplier measured as the piston source is moved along the tube. The mean current, $\bar{i}_{piston}$, can be determined, and an equivalent mean position in the tube found. This position represents the position at which a disc layer of light such as the piston source may be placed to simulate a uniform volume of radiators filling the entire flow tube. That is, the current in the photomultiplier, i_Δ, obtained when $O_2(^1\Delta)$ fills the cylindrical volume, can be converted to an absolute value (photons/sec) by comparison with $\bar{i}_{piston}$. Hence the concentration of $O_2(^1\Delta)$ can be calculated.

The calculation proceeds as follows:

The irradiance of the standard source at 100cm is

$$I_{std}^{100} = I_{std}^{40} \left(\frac{40^2}{100^2}\right) \mu W/cm^2/10\text{Å} \qquad \text{(B1)}$$

Hence the irradiance of the piston source at 100 cm is

$$I^{100}_{piston} = \left(I^{40}_{std}\right)\left(\frac{40^2}{100^2}\right)\left(\frac{i_{piston}}{i^{100}_{std}}\right)\left(\frac{\delta\lambda}{10}\right) \mu W/cm^2 \qquad (B2)$$

where $\delta\lambda$ represents the band-width in Angstroms of the spectrometer. This can be re-written as

$$I^{100}_{piston} = \left(I^{40}_{std}\right)\left(\frac{40^2}{100^2}\right)\left(\frac{i^{100}_{piston}}{i^{100}_{std}}\right)\left(\frac{\delta\lambda}{10}\right)\left(100^2\right)\frac{\mu W}{steradian} \qquad (B3)$$

because when the spectrometer entrance slit is 100 cm from the piston source, it collects light emitted from the piston source over a solid angle of $\omega = 1/100^2$ steradians.

The $O_2(^1\Delta)$ fluorescence collected at the entrance slit is therefore given by

$$\Delta = \left(\frac{i_\Delta}{\bar{x}\, i_{piston}}\right)\left(I^{40}_{std}\right)\left(40^2\right)\left(\frac{i^{100}_{piston}}{i^{100}_{std}}\right)\left(\frac{\delta\lambda}{10}\right)\frac{\mu W}{steradian} \qquad (B4)$$

Since $O_2(^1\Delta)$ irradiates over a solid angle of 4π, this expression must be multiplied by 4π to obtain the total $O_2(^1\Delta)$ fluorescence in μW. The number, N, of $O_2(^1\Delta)$ molecules irradiating per sec. is therefore

$$N = \left(\frac{i_\Delta}{\bar{x}\, i_{piston}}\right)\left(I^{40}_{std}\right)\left(40^2\right)\left(\frac{i^{100}_{piston}}{i^{100}_{std}}\right)\left(\frac{\delta\lambda}{10}\right)\left(\frac{4\pi}{h\nu_{1.27}}x10^{-6}\right) \qquad (B5)$$

where $h\nu_{1.27}$ is the energy of a 1.27μ photon. The total number of molecules of $O_2(^1\Delta)$ per unit volume, N_v, is

$$N_v = \left(\frac{i_\Delta}{i^{\bar{x}}_{piston}}\right)\left(i^{40}_{std}\right)\left(40^2\right)\left(\frac{i^{100}_{piston}}{i^{100}_{std}}\right)\left(\frac{\delta\lambda}{h\nu_{1.27}}\,10^{-6}\right)\left(\frac{\tau}{v\ \ln 2}\right) \quad \text{(B6)}$$

where τ = halflife of $O_2(^1\Delta)$ in seconds, and V = the cylindrical tube volume in cm. This number can readily be converted to a pressure, P, in torr, using the Lochsmidt Number, $L=2.7\times10^{19}cm^{-3}$. Then

$$P = \left(\frac{760}{2.7\times10^{19}}\right)\left(\frac{i_\Delta}{i^{\bar{x}}_{piston}}\right)\left(I^{40}_{std}\right)\left(40^2\right)\left(\frac{i^{100}_{piston}}{i^{100}_{std}}\right)\left(\frac{\delta\lambda}{10}\right)$$

$$\left(\frac{4\pi}{h\nu_{1.27}}\,10^{-6}\right)\left(\frac{\tau}{V\ \ln 2}\right) \quad \text{(B7)}$$

torr of singlet delta molecular oxygen, or

$$P = 1400\ \left(I^{40}_{std}\right)\left(\frac{\delta\lambda}{V}\right)\left(\frac{i_\Delta}{i^{\bar{x}}_{piston}}\right)\left(\frac{i^{100}_{piston}}{i^{100}_{std}}\right)\ \text{torr} \quad \text{(B8)}$$

In the present experiments, values for the parameters in (B8) are typically I^{40}_{std} = 5.725/μW/cm^2/10A; $\delta\lambda$ = 155A; V = 1104 cm^3 $i^{\bar{x}}_{piston} = 5.85 \times 10^{-10}$A; and $\left(i^{100}_{piston}\right) / \left(i^{100}_{std}\right) = 0.00871$;

so that

$$P = 1.67 \times 10^{10}\ i_{\Delta}\ \text{torr} \qquad \text{(B9)}$$

i.e., A photomultiplier current of 1 picoamp produced by $O_2(^1\Delta)$ fluorescence corresponds to an $O_2(^1\Delta)$ pressure of about 10^{-2} torr.

APPENDIX C

P-N DETECTORS FOR SINGLET-DELTA OXYGEN MOLECULES

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1. INTRODUCTION

The p-n detectors described in this report have been designed and fabricated for the detection of singlet delta oxygen. The detector is formed by a lightly doped n-type epitaxial layer on a heavily doped p-type silicon substrate. The theory suggests that under a forward bias, the holes from the substrate will be transported across the junction to the device surface where they will be liberated by excited oxygen of any is available. As the device may need to be operated while immersed in a liquid, it is coated with wax, leaving only the active area exposed. The metal pad and the bonding wire are anodized to give them a dielectric oxide coating. The basic structure of the device has been shown in Fig. C-1.

Some important design considerations, the device fabrication steps and the specifications for the device have been described in the following pages.

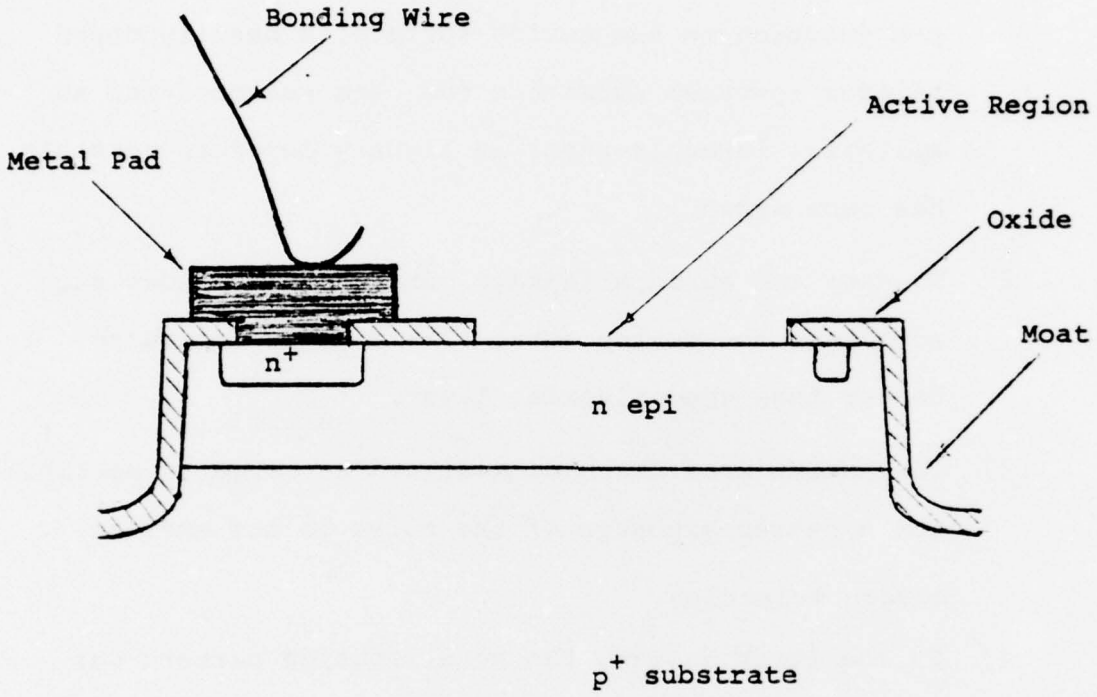


Figure C-1. Basic Structure of Semiconductor Device

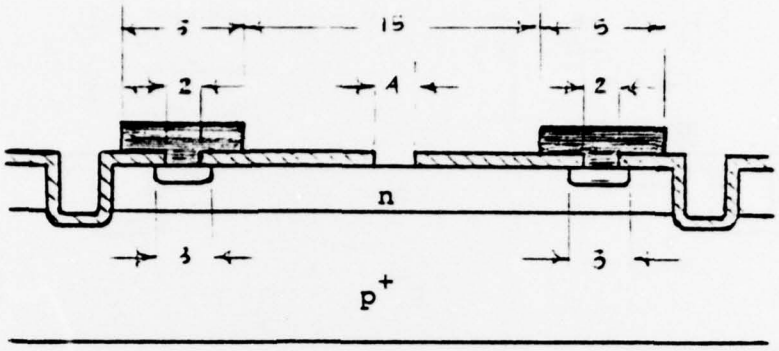
2. DESIGN CONSIDERATIONS

1) For efficient transport of the holes across the p-n junction to the device surface, a heavily doped silicon (p-type) substrate has been selected and an epitaxial layer (n-type) as lightly doped as possible has been grown.

2) To keep the surface leakage current low, a moat etch surrounds the device area. The moat is of course deeper than the epitaxial layer.

3) The active area has been designed as large as possible for a better exposure of the holes to the excited oxygen molecules.

4) In the first design, the metallization pattern was made to surround the active area. This was found to create inconvenience in coating the metallization pattern with wax without harming the active region. (See Fig.C-2) In the revised design, therefore, the metallization pattern has been kept at a corner of the active region. (See Fig.C-3)



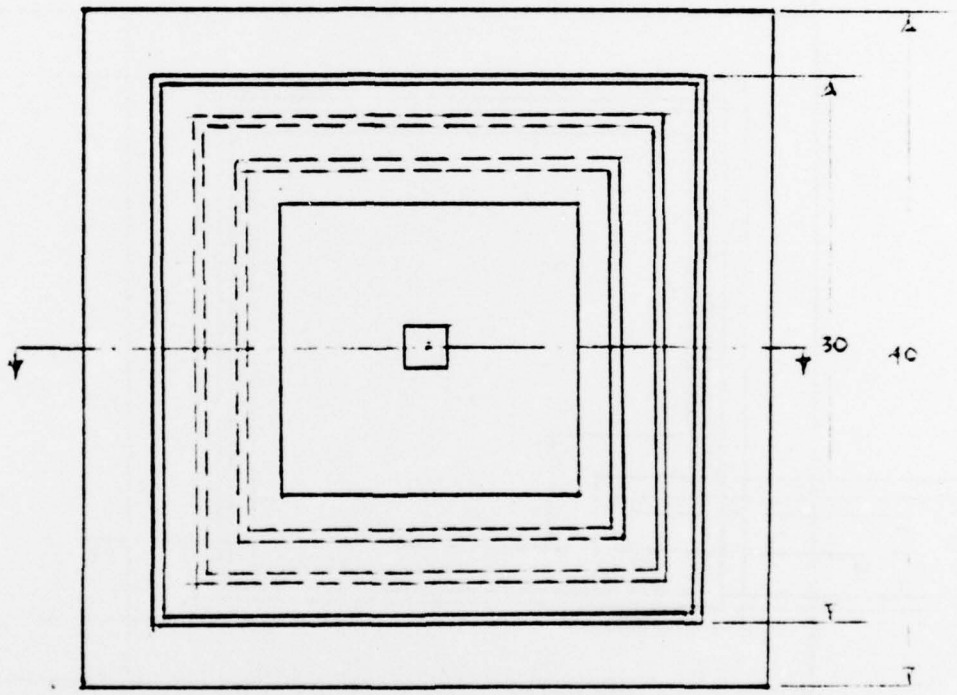


Figure C-2. Device Dimensions (first design) in mils

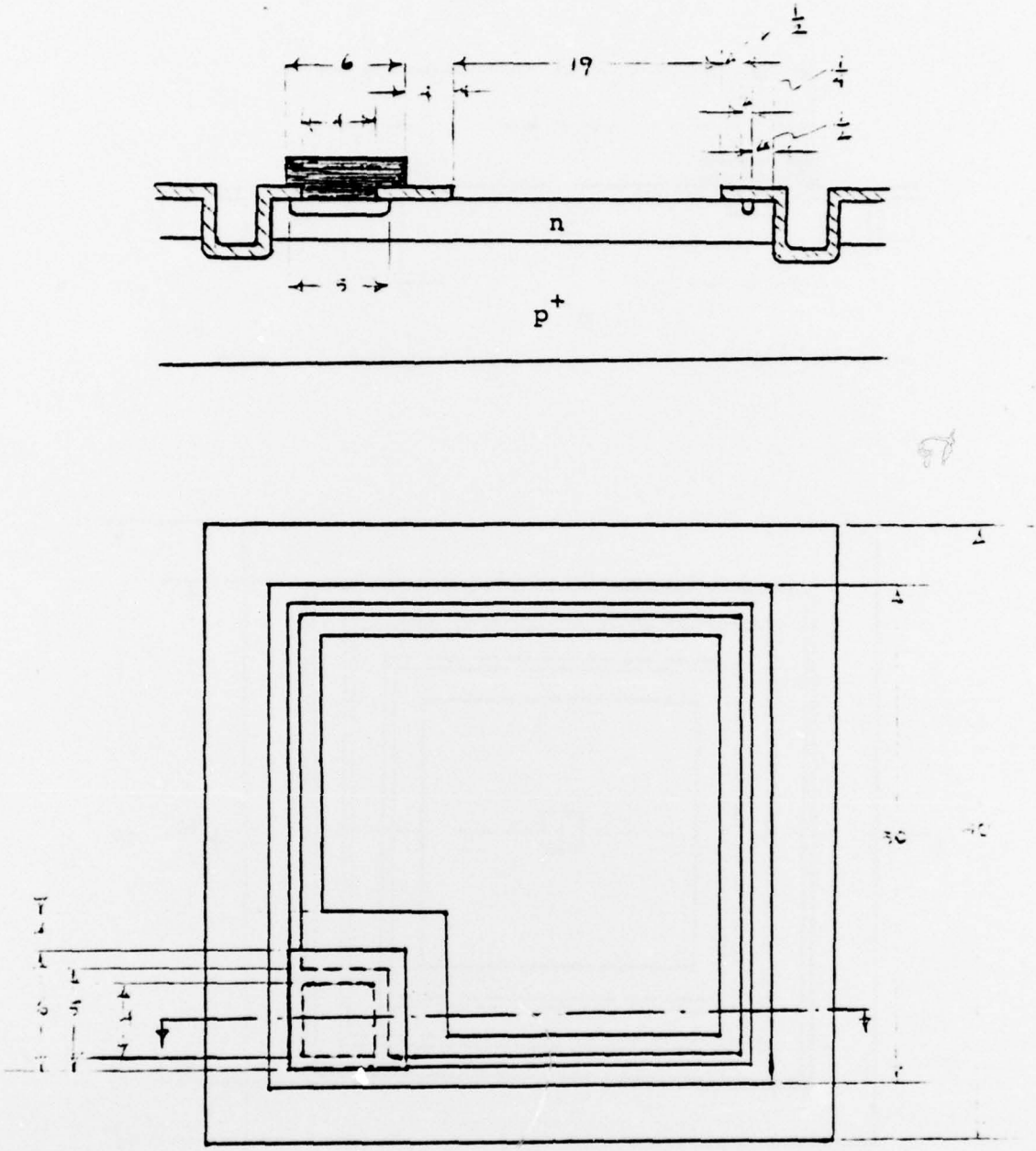


Figure C-3. Device Dimensions (second design) in mils

3. FABRICATION STEPS

1) The p-type silicon wafer is cleaned and prepared for the epitaxial reactor. This involves growing an oxide layer on the wafer and etching it just before putting in the epi tube. (Fig. C-4)

2) An n-type epitaxial layer is grown on the silicon substrate.

3) An oxide of thickness up to 3000-4000Å is grown

4) Using photolithographic techniques, windows for the moat etch are opened and moats are etched, taking care that the moat is deeper than the epitaxial layer. (Use mask #1 of Fig. C-5)

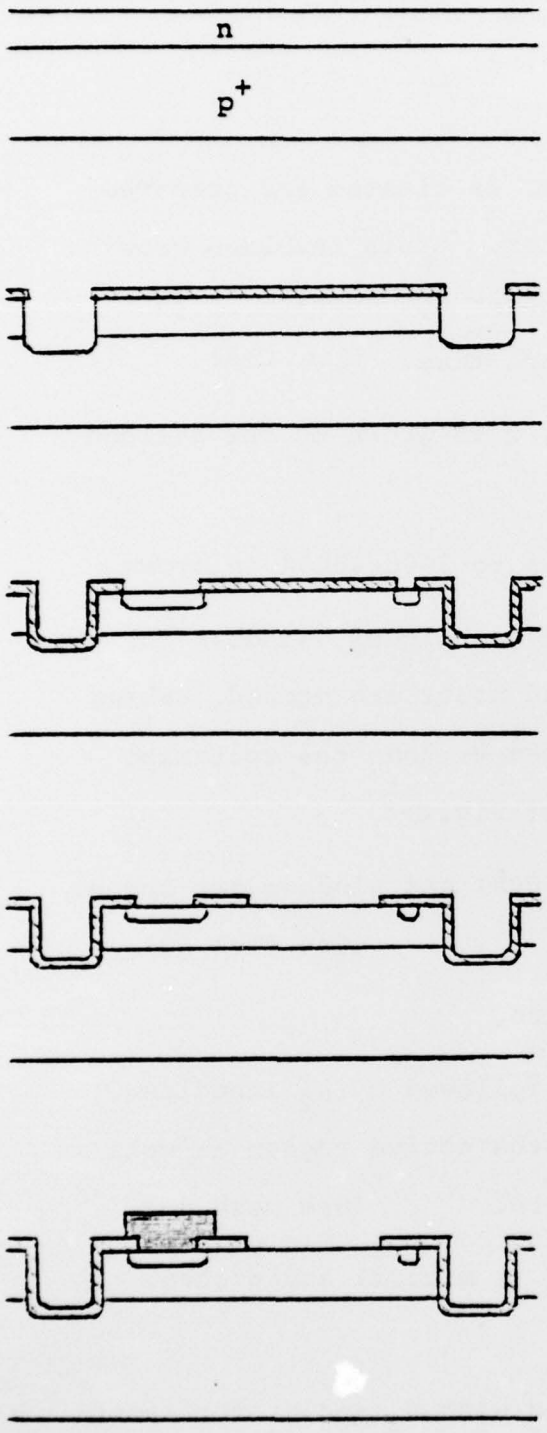
5) Oxide is grown (2000-3000Å) and windows are opened for the n^+ diffusion. (Use mask #2)

6) Phosphorus predep is done.

7) Oxide is grown (2000Å) followed by N_2 annealing. Windows are opened for the active region as well as the metallization pattern. (Use mask #3)

8) Alluminum is evaporated (1 micron) and etched. (Use mask #4)

9) The devices are annealed with H_2 and N_2 for about 30 minutes.



a. Epitaxial growth

b. Moat etch (Mask #1)

c. n^+ Pre-dep (Mask #2)

d. Oxide cuts (Mask #3)

e. Metallization (Mask #4)

Figure C-4. Device Fabrication Steps

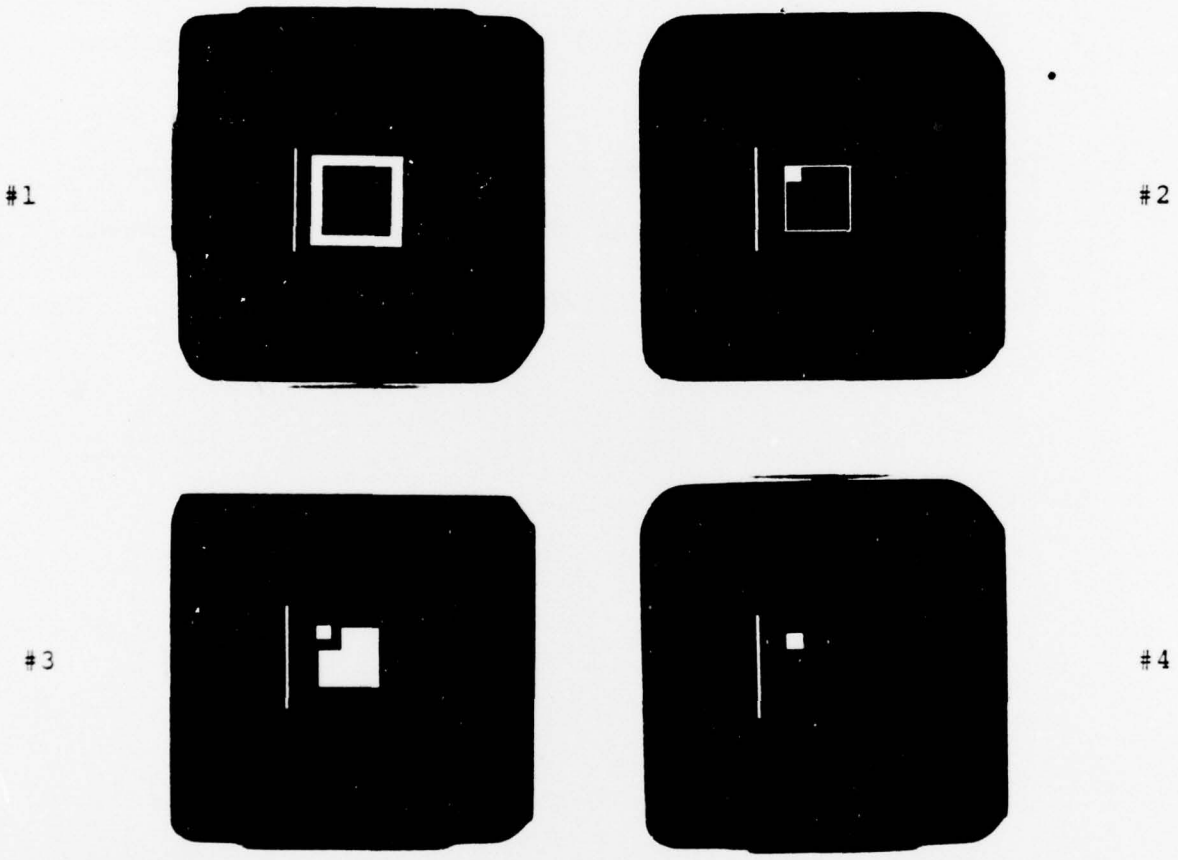


Figure C-5. Masks Used for Device Fabrication

10. The wafer is cleaved for each device as close as possible to the outside edge of the moat. Then the devices are mounted on separate headers using epoxy.

11. The aluminum pad of the device is connected to the header post by bonding a wire using the ultrasonic bonder.

12. The header is coated with wax leaving the active region, the metal pad and the bonding wire exposed.

13. The aluminum is anodized.

4. SPECIFICATIONS

Substrate ... 1-1-1 , 1.0 ohm-cm. , p-type

Epi Layer ... V/I = 1200 ohm, 2.2 ohm-cm., 4 micron

n^+ Predep ... V/I = 2.0 ohm.

SEM test performed to compare junction depth and moat depth showed that moat was deeper than the epi layer.

Typical Saturation Current ... I_{sat} = 1.0 microamp.

Typical Reverse Breakdown Voltage ... V_{BR} = 25 - 70 V

Diode Characteristics are shown in Figs. C-6 and C-7.
A photomicrograph of the device is shown in Fig. C-8.

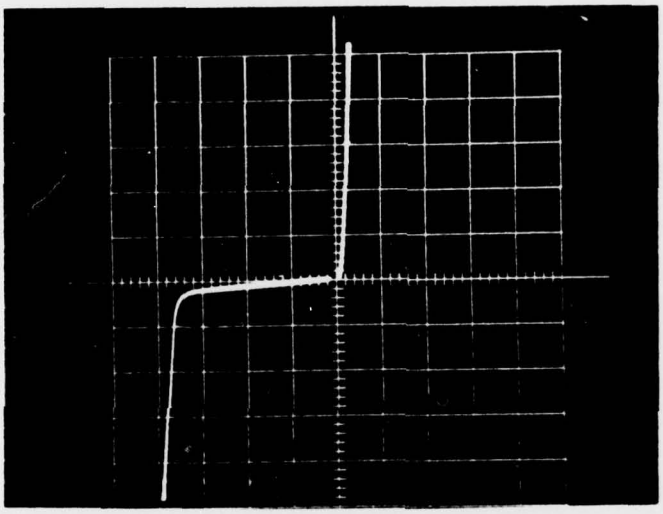


Figure C-6. I-V Characteristics of the Device

I - 0.02 mA/large div.
V - 20 V/large div.

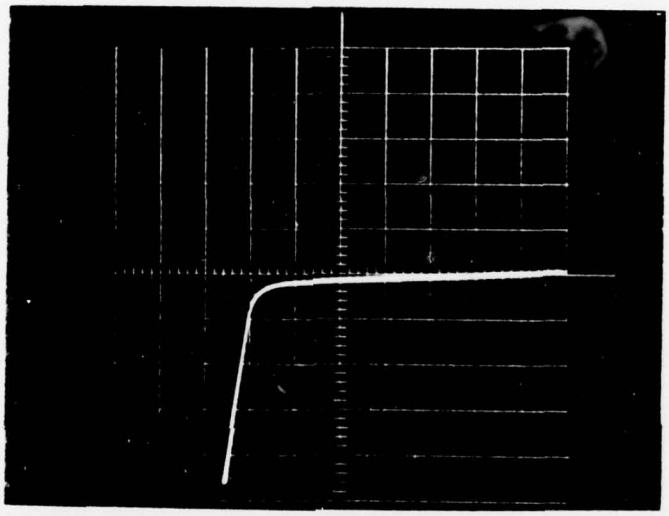


Figure C-7. Reverse Characteristics of the Device

I - 0.02 mA/large div.
V - -10 V/large div.

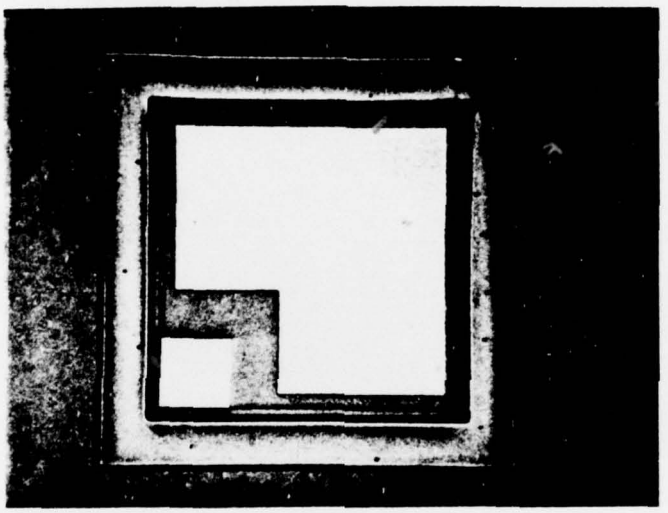


Figure C-8. Photomicrograph of the Device

APPENDIX D

MASS SPECTROSCOPIC DETERMINATION OF O_2/N_2 RATIO

In order to verify the amount of total oxygen produced during the operation of the chemical generator, batch samples were taken during several experiments and were analyzed to determine the ratio of O_2 to N_2. From the knowledge of the total $O_2 + N_2$ pressure in the sample cell, the O_2 partial pressure could be determined.

The sample cell consisted of a 500 ml flask fitted with a 4 mm viton and Teflon vacuum and stopcock and was connected to the chemical generator by an ultratorr fitting for ease of removal. The sampling site was located on the output side of the piston source measuring tube.

After a sample was taken and the run completed, the bulb was connected to one side of the differential Baratron manometer and the condensables removed by cooling the sample bulb's cold finger with ℓN_2. The total ($N_2 + O_2$) pressure was then measured. The volume of the Baratron was small compared to that of the sample bulb, so that the Baratron pressure read low by only a few percent.

The sample was then taken to a mass spectrometer (MS-10) and an air calibration scan was taken, followed by a scan of the actual sample. The air sample allowed the determination

of the relative peak heights of O_2 and N_2, with the ratio O_2/N_2 being taken as .209/.78. Before each scan the spectrometer was pumped down and a background scan taken. The residual O and N peaks were then subtracted from the peak heights determined on the subsequent run.

The general solution of mass spectrometer determination of O_2/N_2 ratio is readly derived in the following manner. The proportion relating the O_2/N_2 ratio of air to that of the sample can be written:

$$\frac{r^o}{R^o} = \frac{r^s}{R^s} \qquad \text{(D-1)}$$

where: r^o = mass spec. O/N peak height ratio for air

r^s = mass spec. O/N peak height ratio for sample

R^o = natural abundance ratio of O_2/N_2 = 0.268

R^s = O_2/N_2 ratio of sample.

Solving equation (D-1) for R^s yields:

$$R^s = R^o\left(\frac{r^s}{r^o}\right) = 0.268\ \frac{r^s}{r^o} \qquad \text{(D-2)}$$

The two simultaneous equations containing the two experimental quantities are:

$$N_2 + O_2 = P_T \tag{D-3}$$

$$\frac{O_2}{N_2} = R^S \tag{D-4}$$

where N_2, O_2 are the partial pressures of N_2 and O_2 in the sample and P_T is the total (Baratron) sample pressure.

Solving equations (D-3) and (D-4) gives the final result:

$$O_2 = \frac{P_T \cdot R^S}{R^S + 1} \tag{D-5}$$

