NBSIR 76-1000

The Construction, Operation and Performance of a Reactive Gas Generator; with Specific Application to HCHO, CH_3CHO, CH_2CHCHO, SO_2, HCN and HCl Production
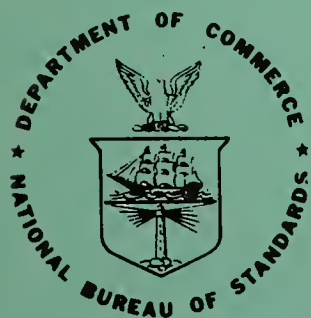
James A. Walker and W. Tsang

Institute for Materials Research
National Bureau of Standards
Washington, D. C. 20234

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THE CONSTRUCTION, OPERATION AND PERFORMANCE OF A REACTIVE GAS GENERATOR: WITH SPECIFIC APPLICATION TO HCHO, CH$_3$CHO, CH$_2$CHCHO, SO$_2$, HCN AND HCl PRODUCTION

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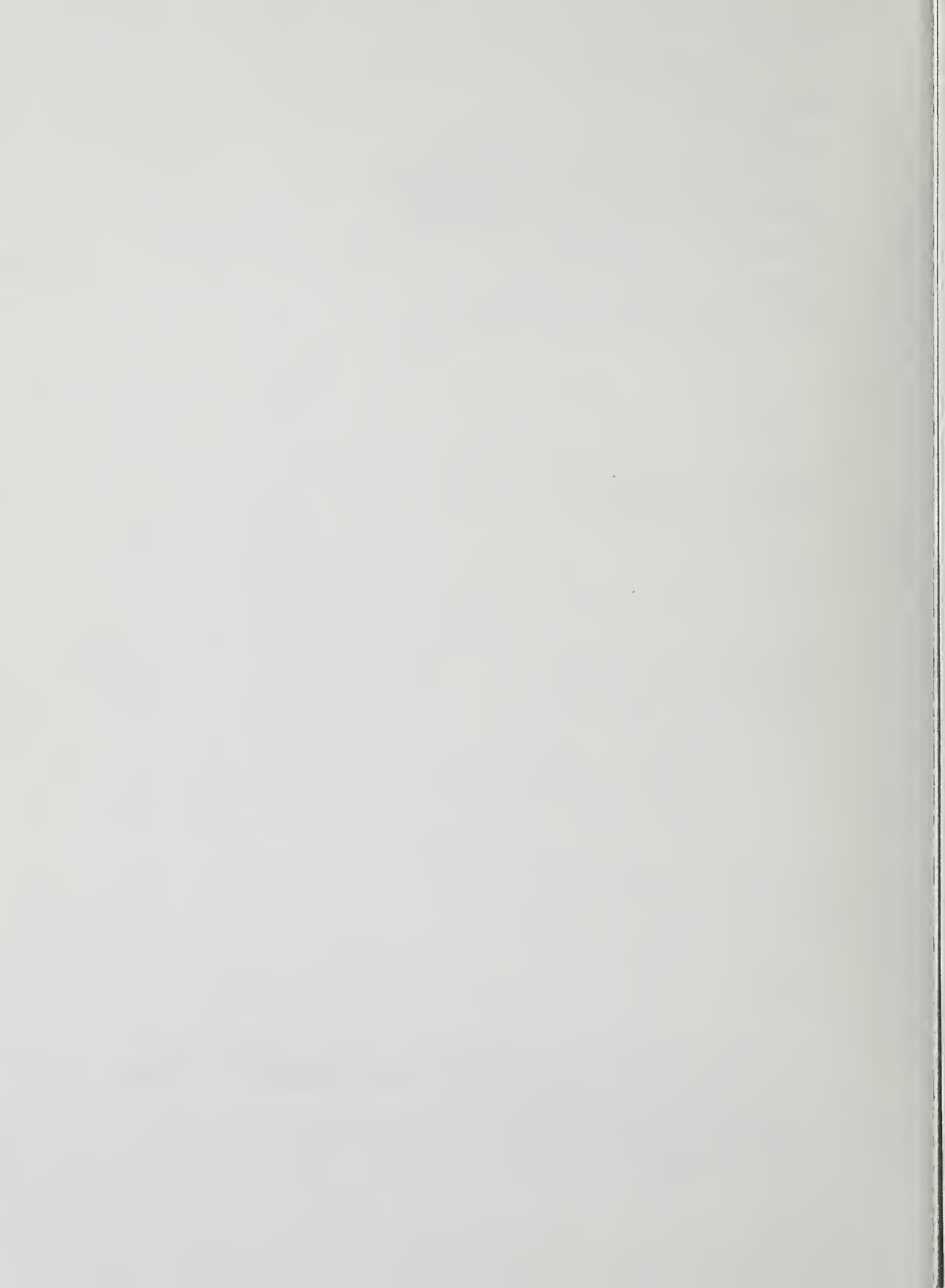January 1976

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The Construction, Operation and Performance of a Reactive

Gas Generator; with Specific Application to HCHO, CH_3CHO,

CH_2CHCHO, SO_2, HCN and HCl Production

James A. Walker and W. Tsang

An instrument capable of generating a variety of reactive gases
in trace levels has been constructed and tested. Operational details,
with specific application to HCHO, CH_3CHO, CH_2CHCHO, SO_2, HCN and
HCl production are discussed.

Table of Contents

Introduction

This report describes the construction, operation and performance of an instrument capable of producing accurate and precise quantities of reactive gases over wide concentration ranges. Possible uses include the calibration of analytical instruments, the evaluation of analytical methodology and the carrying out of toxicity investigations. More specifically, test results on the generation of SO_2, HCHO, HCl, CH_3CHO, HCN and CH_2CHCHO (acrolein) will be summarized.

The reactive nature of the gases which are of concern in pollution, occupational health or toxicological contexts render unsatisfactory standard static methods (1) of sample preparation. Obviously, a dynamic method where the required samples can be prepared immediately prior to use can be expected to circumvent some of these problems. The present instrument is designed to serve this function. It involves, first, the generation of a dilute mixture of a large organic "parent" molecule in an inert diluent through the use of the well established diffusion cell technique (1) and then flowing this mixture through a hot tube where complete stochiometric decomposition occurs and the reactive gas of interest is formed. The "parent" molecule of choice is one that undergoes pyrolytic decomposition <u>exclusively</u> via the reaction

$$\text{parent molecules} \rightarrow \text{hydrocarbon} + \text{reactive compound.}$$
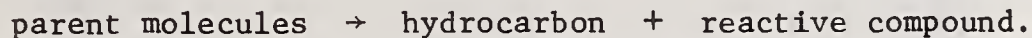
Thus the quantity of the reactive gas delivered to the detector can be deduced from the amount of the hydrocarbon that is present. Calibration of the latter is straightforward. The presence of this internal standard is an added feature since it minimizes the possibility of

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operator error. Furthermore by varying the quantity of the "parent" molecule diffusing into the inert diluent this method has for practical purposes infinite dynamic range. In contrast, the concentration of static samples is always fixed.

Apparatus and Principle of Operation

Front and top views (with instrument open) of the reactive gas generator can be found in Figures I and II. A more detailed photograph of the diffusion cell can be found in Figure III.

Fundamentally, the generator can be considered to be made up of two constant temperature compartments. The first, containing the metal diffusion and buffer cells can be maintained at temperatures from ambient to 250°C. Heat is supplied by a 4 in X 10 in (1 in = 2.54 cm) flexible heater fixed to the bottom of the aluminum box holding the cells. Temperature control of ± 0.1°C is achieved using a RFL-70 controller (2). The second compartment holds the 1/8 in OD gold tubing in which pyrolysis is carried out. A cartridge heater provides the thermal input. The temperature range is from 0 to 760°C and can be held to ± 12°C using a Burling A-1S thermostat. The upper portion or head of the metal diffusion cell contains the diffusion column. A variety of heads, with ID up to 0.25 in maybe used. The length of the diffusion column is of the order of 2.5 in. The substance to be pyrolyzed is placed in a glass cup which sits on the lower portion or base of the diffusion cell. The total volume of sample that can be accommodated is of the order of 15 cc. This is sufficient for practically all conceivable applications. A 0.125 in hole at the bottom of the base of the diffusion
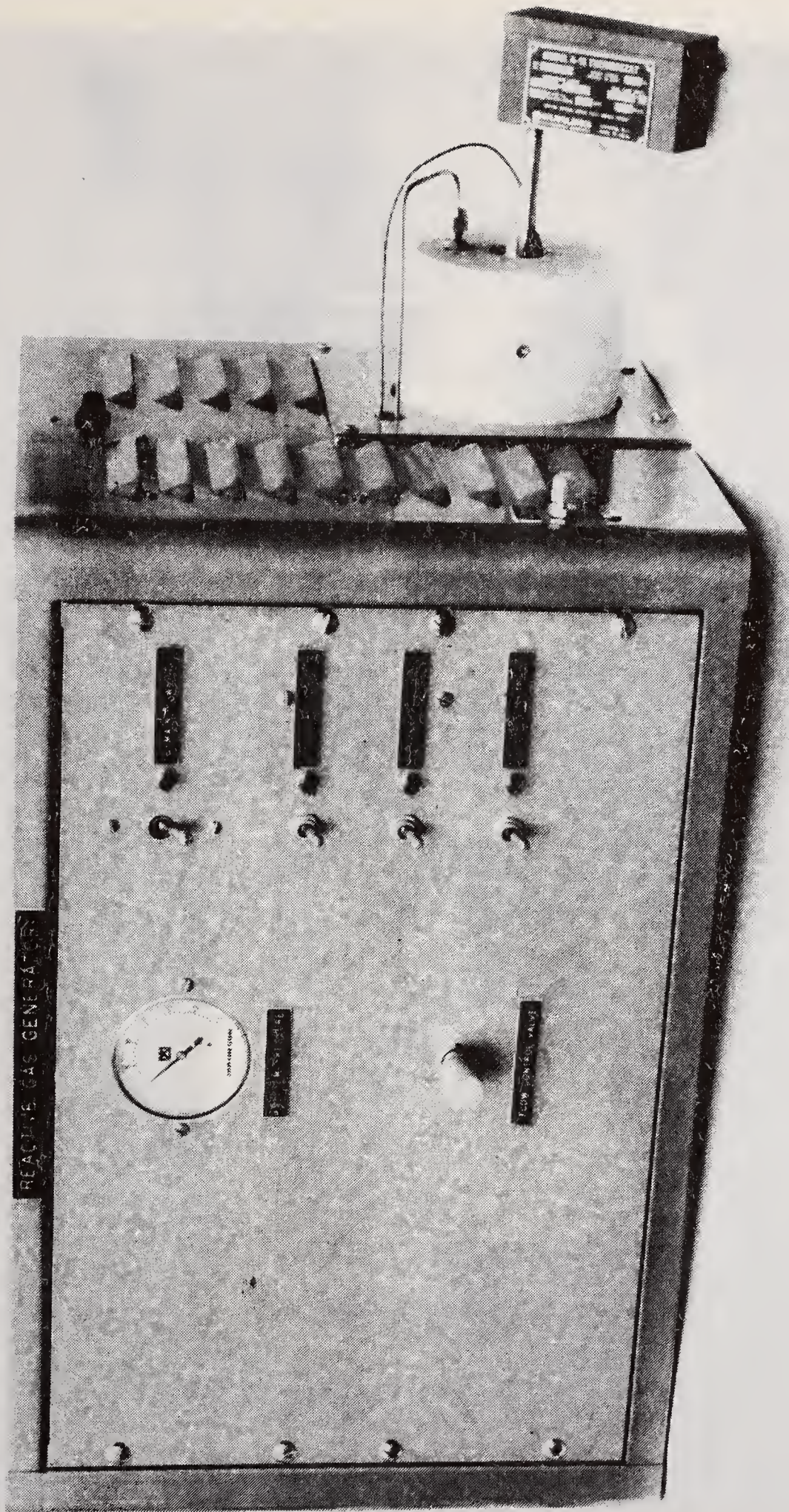
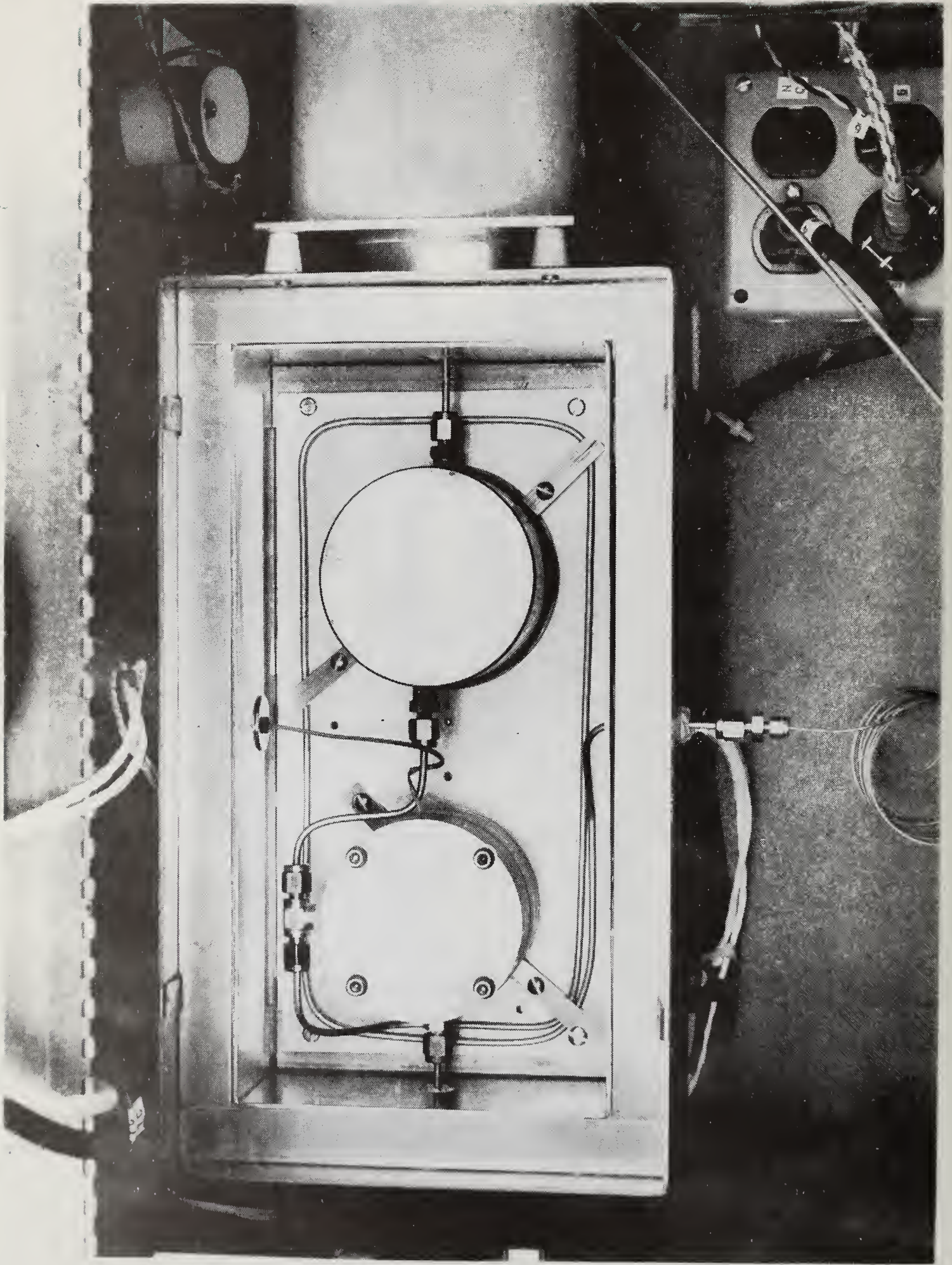FIGURE 1 Reactive Gas Generator (front view.)
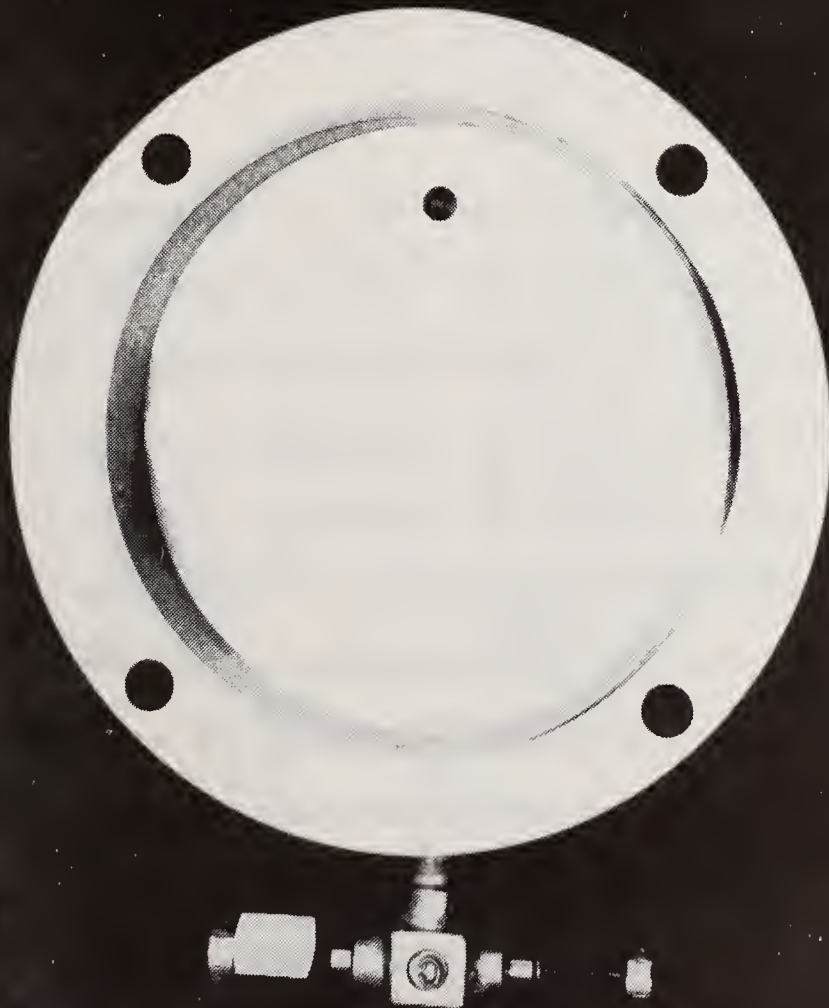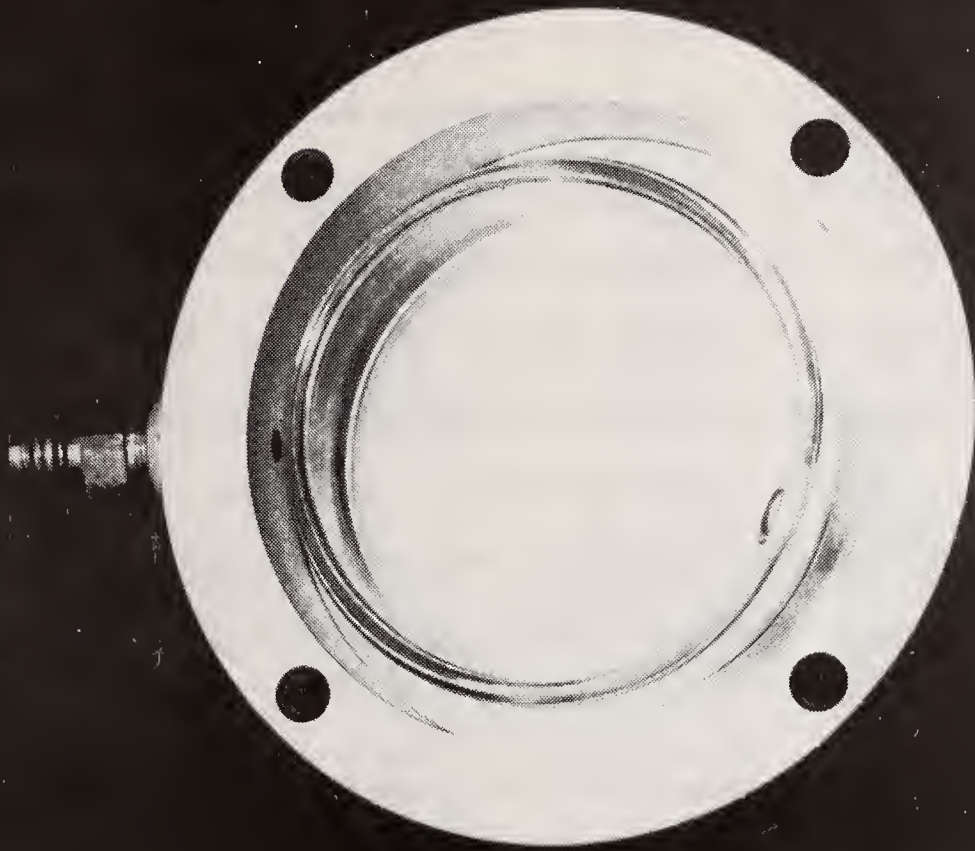
FIGURE 2 Diffusion Cell Compartment (top view.)

FIGURE 3 Diffusion Cell (disassembled).

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cell provides a means of purging the cell of air so that oxidation will not make any contribution to the pyrolytic process. The role of the buffer cell is to take out pressure surges which arises from the switching of valves or the connection of fittings. The entire system is operated at about 1/2 atmosphere above ambient pressure. Control is effected by means of a needle valve at the exit of the pyrolyzer. This has the advantage of decoupling the system from downstream events. It also makes it easy to check for leaks in the system. Experience from these studies suggests that this is the most likely source of error using this device. Detailed drawings of the instrument can be found in Figures IV to VII.

The relationship between the diffusion rate and the physical parameters of the material and the diffusion cell is

$$Q_d = \frac{DA}{L} \ln \left(\frac{P}{P-P_v}\right) \quad (1)$$

where Q_d = diffusion rate, volume/time, D = diffusion coefficient, A = diffusion tube cross-section, L = diffusion tube length, P = pressure in diffusion cell and P_v = partial vapor pressure of diffusing vapor. It is important to note that the diffusion rate can be varied by changing the diffusion tube cross-section A and/or by changing the cell temperature. The latter arises from the three-halves power dependence of the diffusion coefficient on temperature (approximate) and the exponential relationship between vapor pressure and temperature (Clapeyron Equation). For vapor pressures sufficiently lower than the cell pressure this is equivalent to an exponential dependence between diffusion rate and temperature. Thus by suitable adjustment of the physical parameters an enormous range of diffusion rates can be

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DRILL (4)NO.11 CLEARANCE
HOLES ON 2-7/8"B.C.

DRILL 1/8"HOLE 2-1/2" DEEP
FOLLOWED BY 11/32" HOLE 3/8" DEEP
TAP 1/8-27 PIPE THREAD

MATERIAL: BRASS, ROD, 1/2 HARD,
COMP. NO.22

DIFFUSION HOLE ROTATED 45° CW
FOR CLARITY

CELL TOP

DRILL (4) NO.21 HOLES 3/8" DEEP
ON 2-7/8" B.C.
TAP FOR 10-32 SCREWS

1/8" GROOVE

1/4-20 THREAD
ALIGNMENT PIN

1/8-27
PIPE THREAD
5/16"DEEP

ROTATED 45° CW
FOR CLARITY
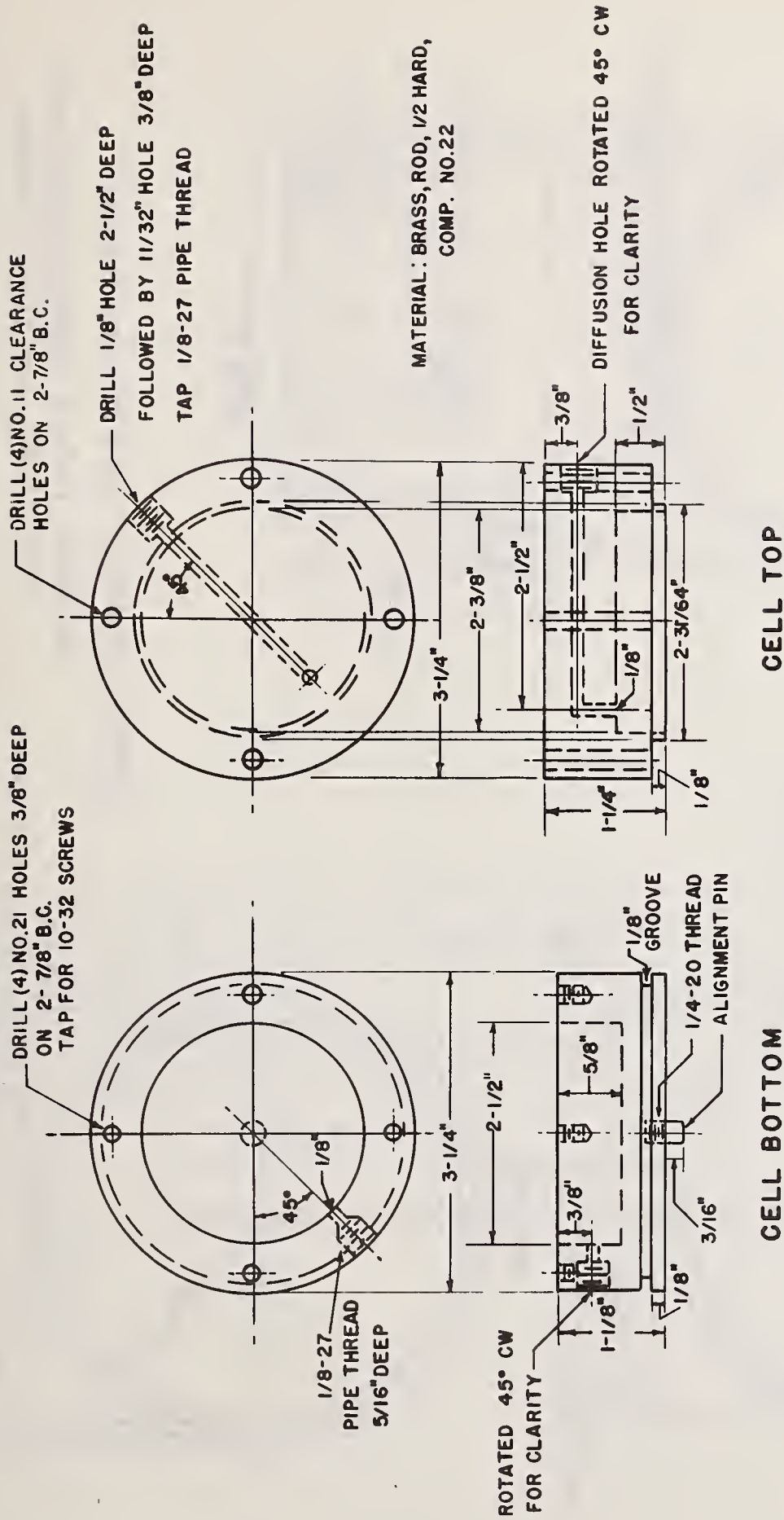
CELL BOTTOM

FIGURE 4   Brass Diffusion Cell

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TOP

BOTTOM

CELL BODY

3-1/2"

3-1/4"

2-1/8"

3/4"

1/2"

B

3-1/2"

3-1/4"

1/8"

1/16"

3-3/4"

3-1/2"

1/8"

1/16"

1-5/8" rad.
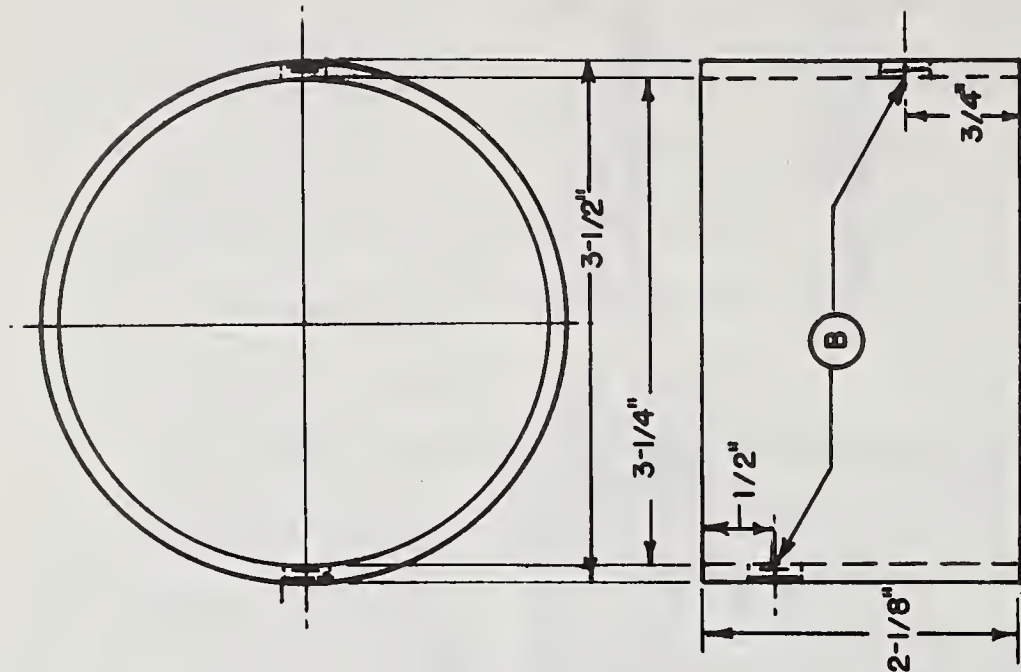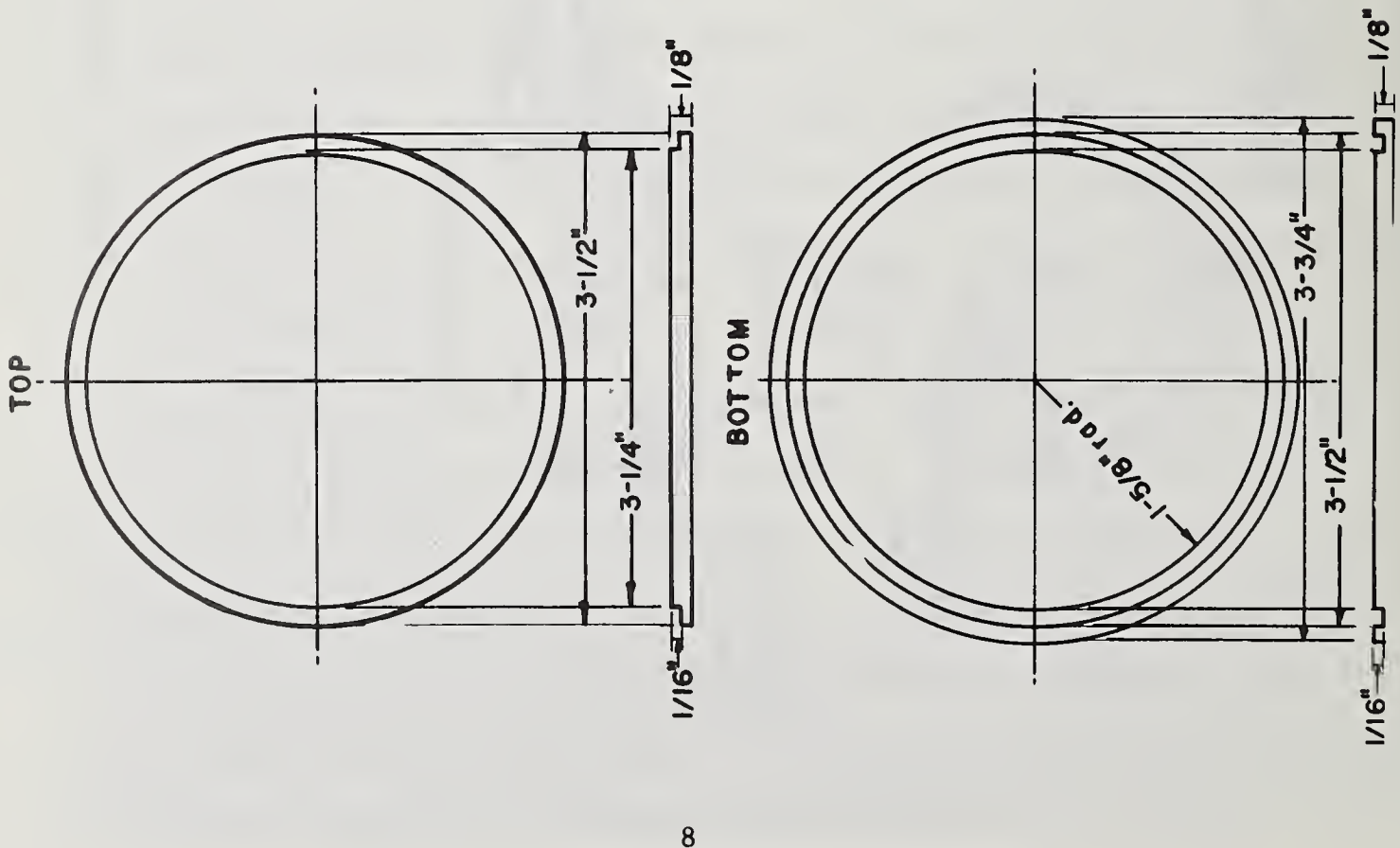
NOTE: (A) BRAZE TOP & BOTTOM TO BODY

(B) BRAZE 1/8" S.S. SWAGELOK MALE PIPE
CONNECTORS (1/8-27 PIPE THREAD)

FIGURE 5   Brass Buffer Cell.

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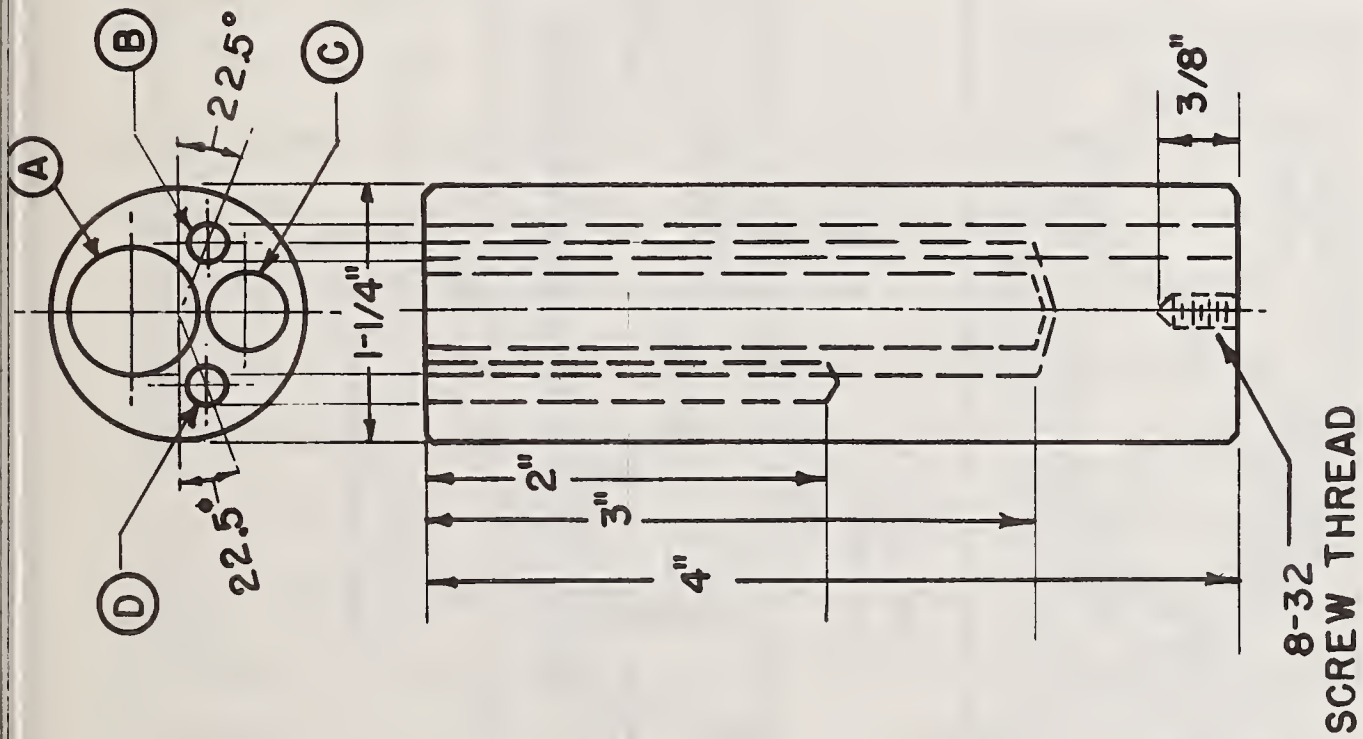
NOTE:

(A) .625" ON 1/4" RADIUS

(B) .199" ON 3/8" RADIUS

(C) .391" ON 5/16" RADIUS

(D) .199" ON 3/8" RADIUS

MATERIAL : MONEL

8-32
SCREW THREAD

3/8"

2"

3"

4"

1-1/4"

22.5°

22.5°

(A) (B) (C) (D)

FIGURE 6   Furnace Heater Block.

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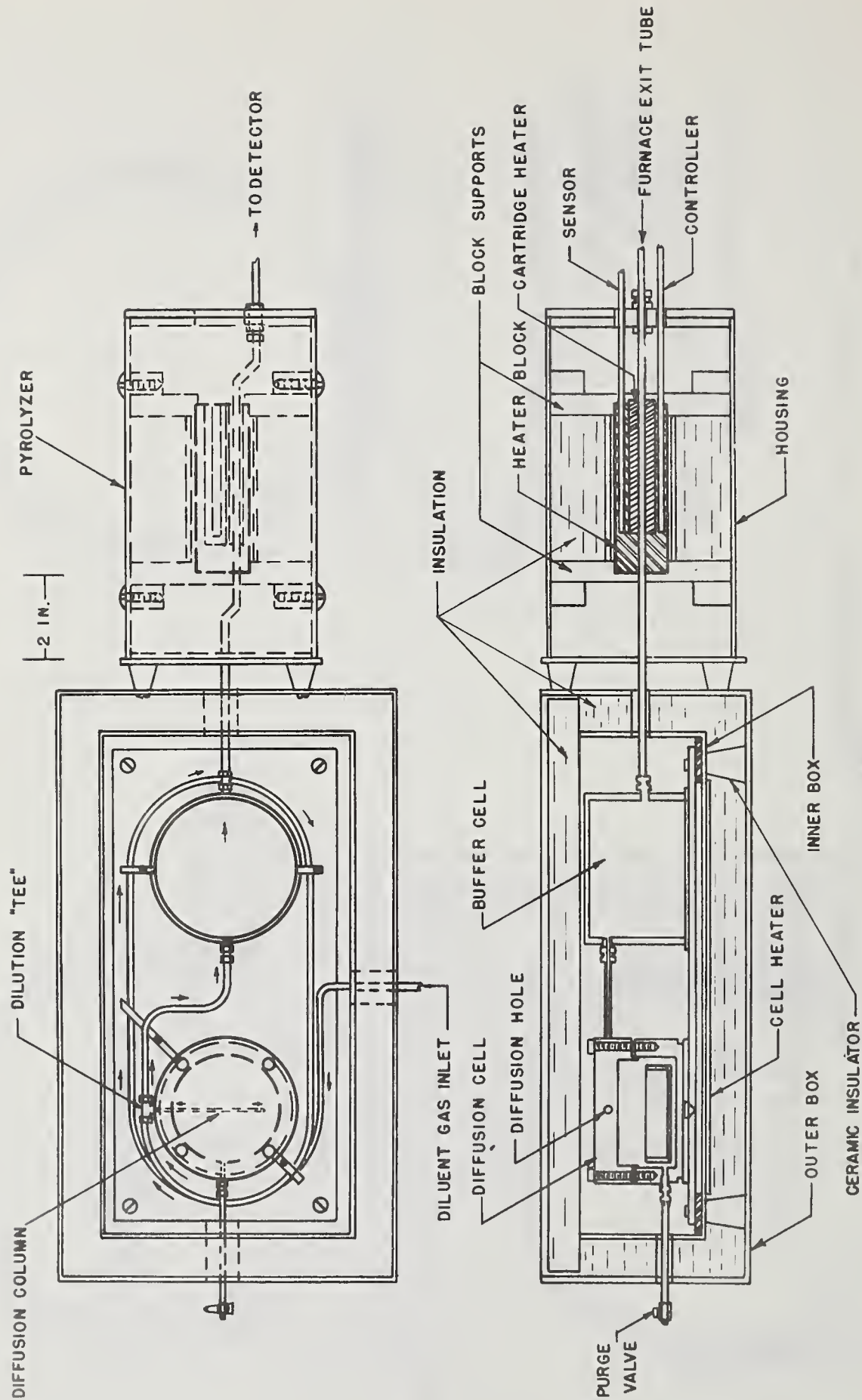
FIGURE 7 Sectional view of Diffusion Cell and Pyrolyzer.

generated. Inversely, this means that for a given range of diffusion

rates the present apparatus can accommodate a wide variety of substance

through the proper selection of diffusion cell cross-section and

temperature. The sensitivity of the diffusion rate to the latter

makes necessary satisfactory controls ($\sim 0.1°C$) on diffusion cell

temperature. On the other hand it also means that diffusion rate

can be set easily and continuously over a wide range. This is in

contrast to the situation for generation from static methods.

Finally, it will be noted that the concentration of reactive gas

in related to the diffusion rate by the equation

$$C = Q_d/Q$$

where Q is the flow rate across the diffusion cell. Thus the concentration

can also be controlled by the flow rate.

The compounds of choice for the present application are those

which decompose unimolecularly into molecular fragments and which

do not have significant side reactions. The avoidance of surface or

chain induced decomposition processes is of prime importance. These

processes are frequently irreproducible and thus completely unsuitable

for the present purposes. This is the reason for the use of the

gold reactor. An excellent source for possible "parent" molecules

is the review by Benson and O'Neal (3). The unimolecular nature

of these reactions dictate that the extent of conversion is

dependent only on the reaction time (t), temperature (T) and the

thermal stability of the appropriate compound. The relation is

$$\ln C_i/C_f = t \, A \, \exp(-E/RT)$$

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where A and E are Arrhenius parameters for unimolecular decomposition

reaction (3) and characteristic of the compound of interest and C_i and C_f

are the initial and final concentrations. In the present context interest

is focused in the region of high conversions or where C_i/C_f is greater

than 50. Thus $C_i \simeq$ concentration of reactive gas. Under these

conditions the concentration of products is relatively insensitive

to changes in reaction variables. Thus these variables need not be

strictly controlled and the operational procedure to locate the

minimum necessary temperature is to increase the pyrolysis

temperature until the product yield reaches a maximum and/or when

the parent molecule disappears.

Identification of Controls and Connections

A.   Front panel

There are three convenience outlets inside the cabinet.
Each outlet is wired independently and is controlled by the appropriate
switch on the front panel. A wiring diagram can be found in Figure VIII.

1.   Main power switch

This switch is in series with and ahead of the other
switches.

2.   Cell heater switch

The cell temperature controller, which is mounted under
the cabinet lid, has a convenience outlet for the cell heater and
a jack for the cell temperature sensor. The controller is
plugged into the outlet controlled by the cell heater switch.

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FIGURE 8 Wiring Diagram.
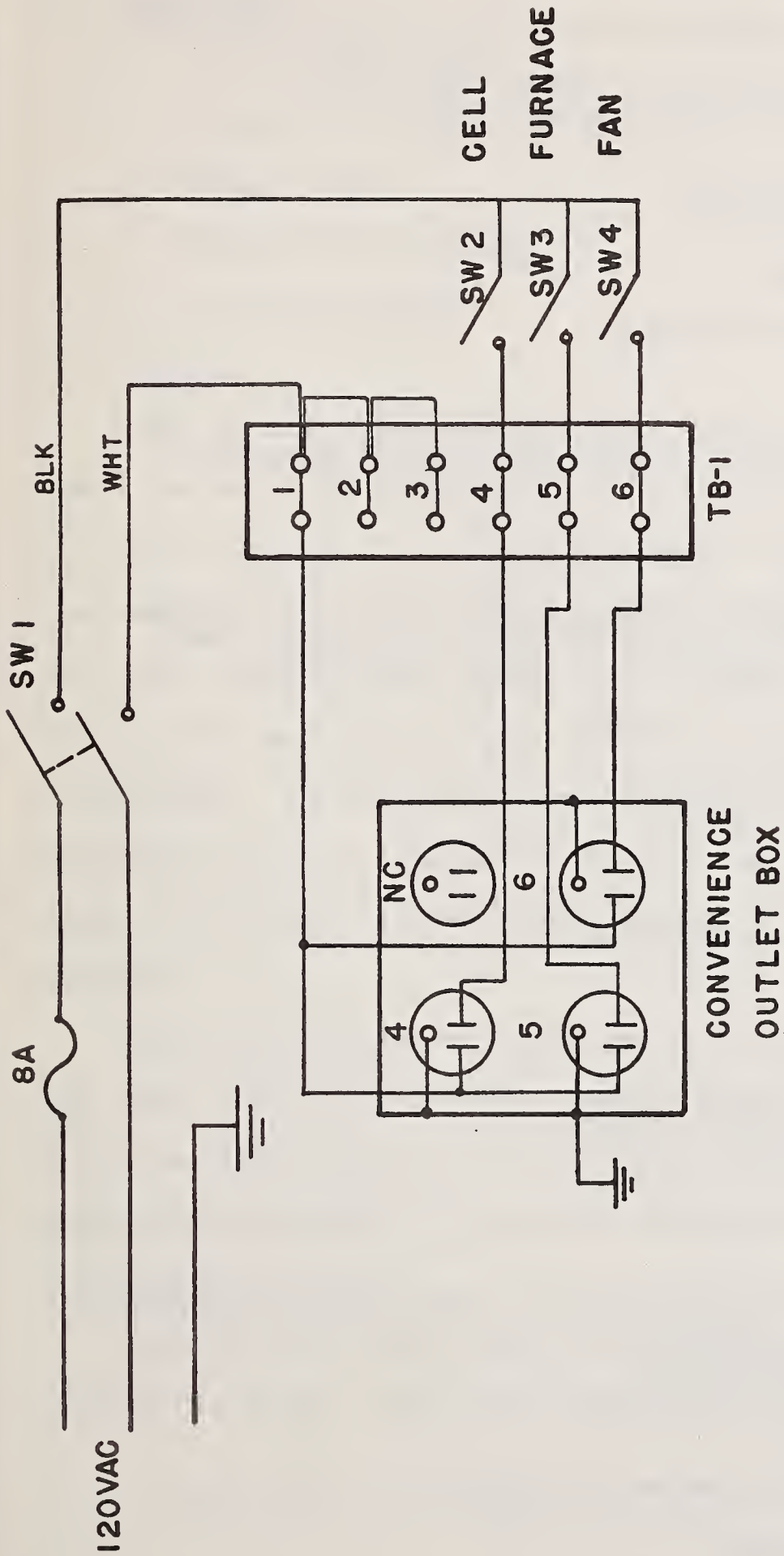
OUTLETS

4 — CELL TEMP. CONTROLLER & HEATER

5 — FURNACE TEMP. CONTROLLER & HEATER

6 — COOLING FAN

3.   Furnace heater switch

The furnace temperature controller and heater are plugged into the outlet controlled by the furnace heater switch.

4.   Fan switch

Operates cooling fan.

5.   Pressure gauge

Indicates system pressure.

6.   Micrometer

The handle of the micrometering valve for flow control.

B.   Left Side Panel

1.   Purge valve

Allows diffusion cell to be purge by directing diluent gas through the cell.

2.   Purge outlet

Cell vent during purge.

3.   Inlet

Connection for diluent gas.

C.   Right side panel

1.   Outlet

Exit for pyrolysis products.

D.   Rear panel

1.   Cell T.C.

Binding post for monitoring the diffusion cell temperature with chromel-alumel thermocouple.

2.   Furnace T.C.

Binding post for measuring temperature of furnace with chromel-alumel thermocouple.

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A.   Requirements

    1.   120V AC power source.

    2.   Diluent gas cylinder with two stage regulator.

    3.   Exhaust vent.

    4.   Detector G.C., MS. etc.

    5.   Precursor material.

B.   Procedure

Raise the lid of the cabinet to gain access to the cell compartment. Remove the top of the compartment and the insulating panel to reach the cell. To charge the cell with a precursor material loosen the two "Swagelok" nuts on the "tee" attached to the cell. Next remove (4) # 10-32 Allen head cap screws. The cell cover can now be raised with the "tee" acting as a hinge. Exercise care in handling the teflon gasket. Add 10-15 cc of liquid or about 15 grams of solid material to the pyrex container in the cell. Lower the cell cover, replace and tighten the screws, then tighten the "Swagelok" nuts securely.

Connect the cylinder of diluent gas to the inlet, on the left side panel, with 1/8 in OD copper tubing. Connect the purge outlet to an exhaust vent with copper or plastic tubing. The sample outlet on the lower right side panel is connected to the test facility with 1/8 in OD stainless steel tubing.

Open the valve on the diluent gas cylinder and set the pressure regulator to 25 psig. Open the micrometer one complete turn and the

purge valve 1/4 turn ccw. After about 15 minutes close the purge valve. Adjust the micrometer and cylinder pressure to give a flow of 40 cc/min. and a system pressure of about 7 psig. A flow calibration curve is provided which gives approximate control settings for flow rates from 10 to 200 cc/min (He). Use of a bubble flowmeter is recommended for a more accurate determination of flow rates.

Check all connections for leaks with soap bubbles or a commercial liquid leak detector. Tighten any connections that leak. When assured of no leaks replace the insulating panel and the cell compartment cover. Plug in power cord.

Turn on the main power, cell heater and furnace heater switches. Set cell and furnace temperature controllers to the desired temperatures, allowing 2 hours for the system to equilibrate.

Since the cell takes time to equilibrate the cell heater should be left on continuously. The diluent gas should also be flowing through the system. On the other hand, the furnace heater can be turned off each evening and turned on each morning because it requires less time to reach operating temperature. If, however, the temperature of the cell is such that the material used as a precursor is exiting the cell with a vapor pressure higher than that at room temperature it is advisable to keep the furnace heater on continuously also. This is necessary to avoid material collecting in the cool furnace and exit lines.

Service Procedures

A. Replacement of furnace heater

    1. Turn off furnace heater switch.

    2. Unplug heater cable from outlet in the rear of cabinet.

3. Gently pull cartridge heater from furnace.

4. Remove fiberglass insulation carefully.

5. Cut the two heater leads at a length equal to the leads on the new heater.

6. Splice the new heater leads and tape securely.

7. Rewrap heater leads with fiberglass insulation.

8. Push heater into furnace as far as it will go.

9. Plug heater cable into heater outlet.

B. Replacement of cell heater

1. Turn all power off and unplug power cord.

2. Unplug furnace heater cable.

3. Disconnect furnace from buffer cell.

4. Disconnect s.s. exit tube from furnace.

5. Remove furnace from insulators mounted on the side of the outer box of the cell compartment by removing four screws on square flange.

6. Next remove diffusion cell, buffer cell and s.s. tubing from the box.

7. Remove four 8-32 screws holding the cell support plate.

8. Remove the heater cable clamp where the cable passes through the outer box.

9. Carefully lift the inner box making sure there is enough slack in the heater cable and the sensor cable.

10. Remove the flexible heater which is attached to the bottom of the inner box by a thin aluminum cover held by four screws.

11. Slide the fiberglass insulating sleeves away from heater connections and cut the leads of the old heater.

12. Splice the new heater wires to the power lead.

13. Solder and tape the splices.

14. Slide the fiberglass insulating sleeve over the splices.

15. Reverse the above steps to reassemble.

C. Cleaning Diffusion Cell

CAUTION!!

Before attempting to remove the cell for cleaning or changing the precursor material, all switches must be off and the cell and furnace must be at room temperature. The diluent gas supply should be turned off at the cylinder valve.

1. Completely remove the "Swagelok" nuts on the "tee" attached to the cell.

2. Remove the brass "Swagelok" nut from the union on the lower left side of the cell. (purge line).

3. Loosen brass screws on cell hold-down clamps and rotate the clamps 90°.

4. Carefully rotate cell, to free tube connections, and lift out.

5. Place cell in hood and remove 4 # 10-32 Allen head cap screws from the cell cover being careful not to damage the "teflon" gasket.

6. Pour out any remaining material if liquid and rinse with solvent.

7. Apply suction to dry.

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8. If cell contains a solid material it may be necessary to gently warm the cell with an electric heat gun in order to remove it.

9. Rinse with a solvent then wash in soap and hot water.

10. Dry with high pressure air.

11. Rinse with acetone, drain and dry with suction.

D. Cleaning Buffer Cell

Note: The buffer cell normally requires no special cleaning, merely apply suction at the system outlet for 10-15 minutes after the diffusion cell has been disconnected. Under extreme conditions removal may be necessary.

Proceed as follows:

1. Disconnect cell from tube to the furnace.

2. Loosen hold-down clamps and lift out.

3. Run hot water through the cell for several minutes then drain.

4. Rinse with acetone, drain and dry with suction or dry air.

5. Reverse the procedure to reassemble.

6. Always use two wrenches in opposition when tightening or loosening "Swagelok" connections.

E. Maintenance

The system requires no regular maintenance except to replace the diluent gas cylinder occasionally and to recharge the diffusion cell.

Replacement of burned-out heaters is described in the service procedures section above.

When shutting the system down for a week or less turn the main power switch off but allow the diluent gas to continue to flow through the system. Make sure the outlet is vented. For a longer period the diluent gas should be turned off at the cylinder valve and the sample removed from the cell.

Data on Specific Reactive Gases

A) HCHO: The "parent" compound for formaldehyde generation is 3-methyl-3-buten-1-ol. The decomposition reaction is

$$CH_2 = C(CH_3)CH_2CH_2OH \rightarrow iC_4H_8 + HCHO$$
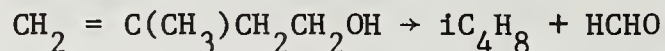
The validity of the postulated stochiometry is established by gas chromatographic analysis of the reaction products with Poropak P-S columns. Since formaldehyde is insensitive to flame ionization detection, conversion to CH_4 (after separation) is effected by passage over nickel catalyst in the presence of hydrogen following the prescription of Stevens, O'Keefe and Ortman (3). The resulting area ratio over the applicable range is 4.22 $\pm$ .12 to 1. The departure from exact 4 to 1 dependence is attributed to substantial tailing in the formaldehyde peak making complete integration difficult. A plot of the results can be found in Figure IX. Maximum thru-put (100% conversion) in terms of formaldehyde output per minute as a function of cell temperature can be found in Figure X. Least squares analysis of the data yields at 7.4 psig and over the temperature range of 30-90°C
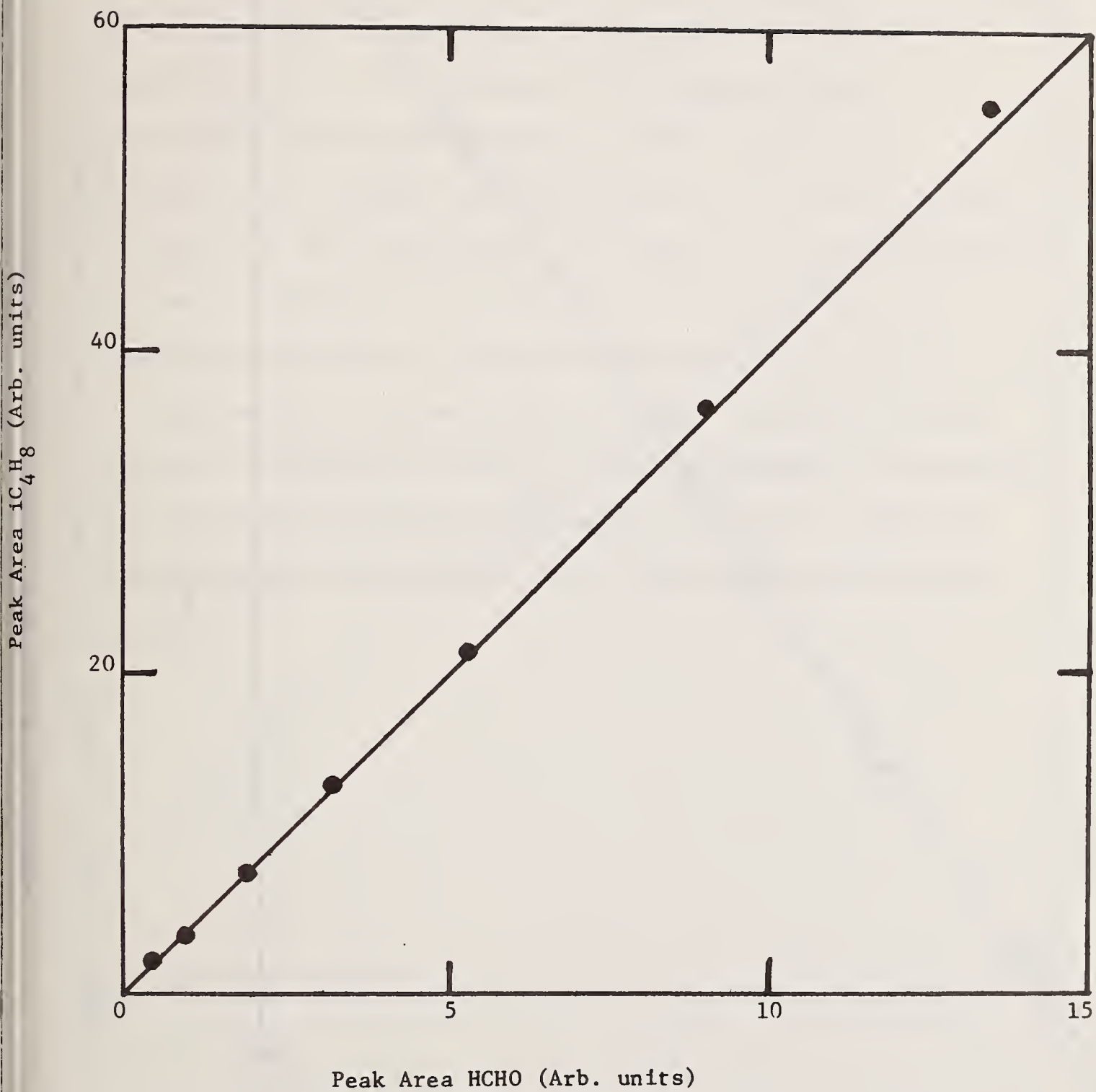
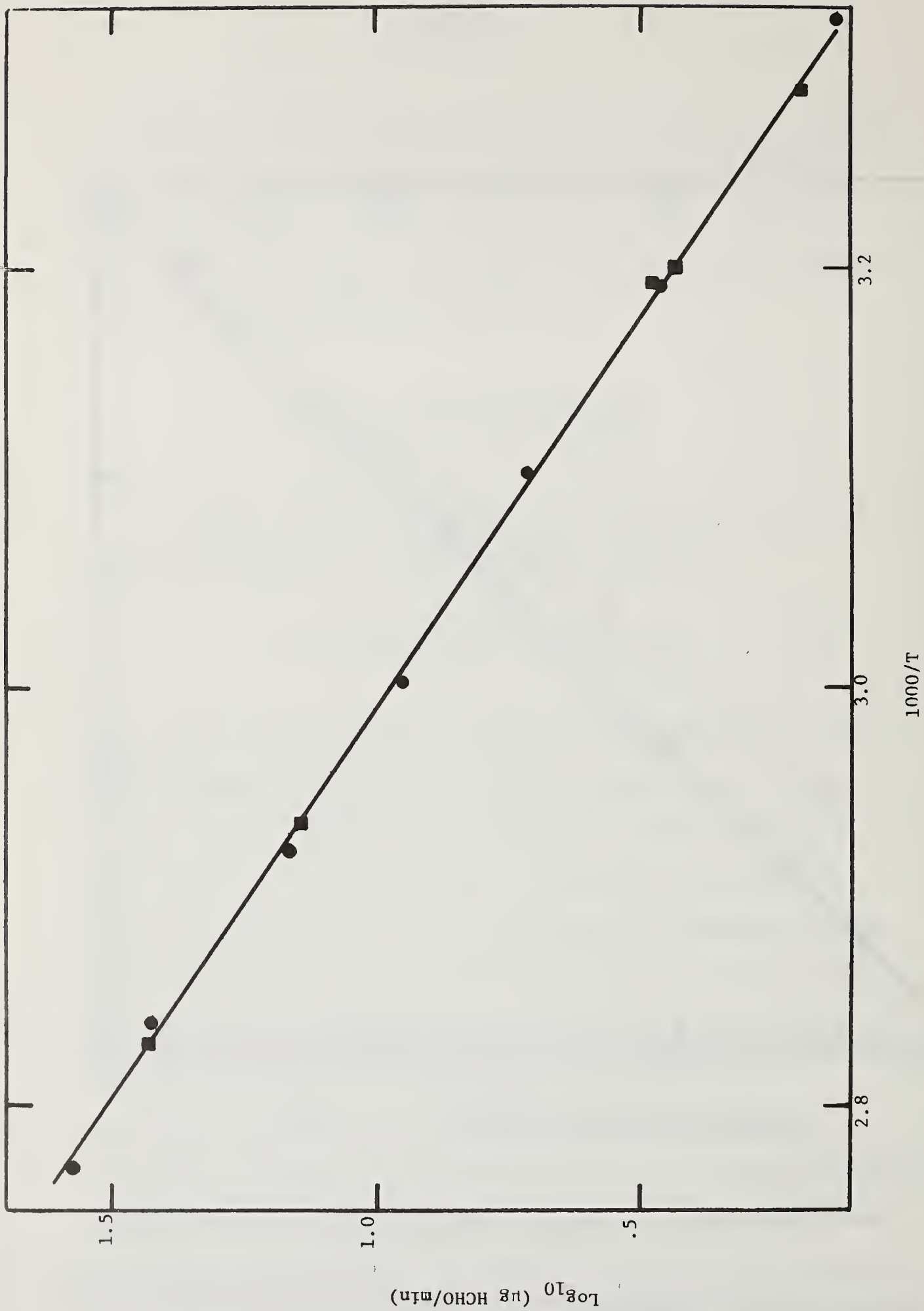FIGURE 9 Relative yields of isobutene and formaldehyde from 3-methyl-3-buten-1-ol.

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FIGURE 10 Yields of HCHO/min from 3-methyl-3-buten-1-ol as a function of temperature. ■ and ● are from different generators.

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$$\text{Log}_{10}[\mu g \text{ HCHO/min}] = -2704.8 \left[\frac{1}{T} \right] + 9.09 \pm .09$$

The thru-put range is 2-50 µg/min. The standard deviation or
"settability" is 4%. With flow rates of 20-200 cc/min (He)
the pyrolyzer temperatures necessary to insure close to 100%
conversion range from 600 to 680°C. Note that at the lowest thru-put
and flow rates small conversions ∿ 5% of HCHO to CO have been observed.
The long term behavior of the generator, and the dependence of
concentration on flow rate and pressure can be found in Table I.

The results of studies carried out using a commercial formalin
solution is summarized in Figure XI. Long term behavior and dependence
of concentration on flow rate is summarized in Table II. Note that
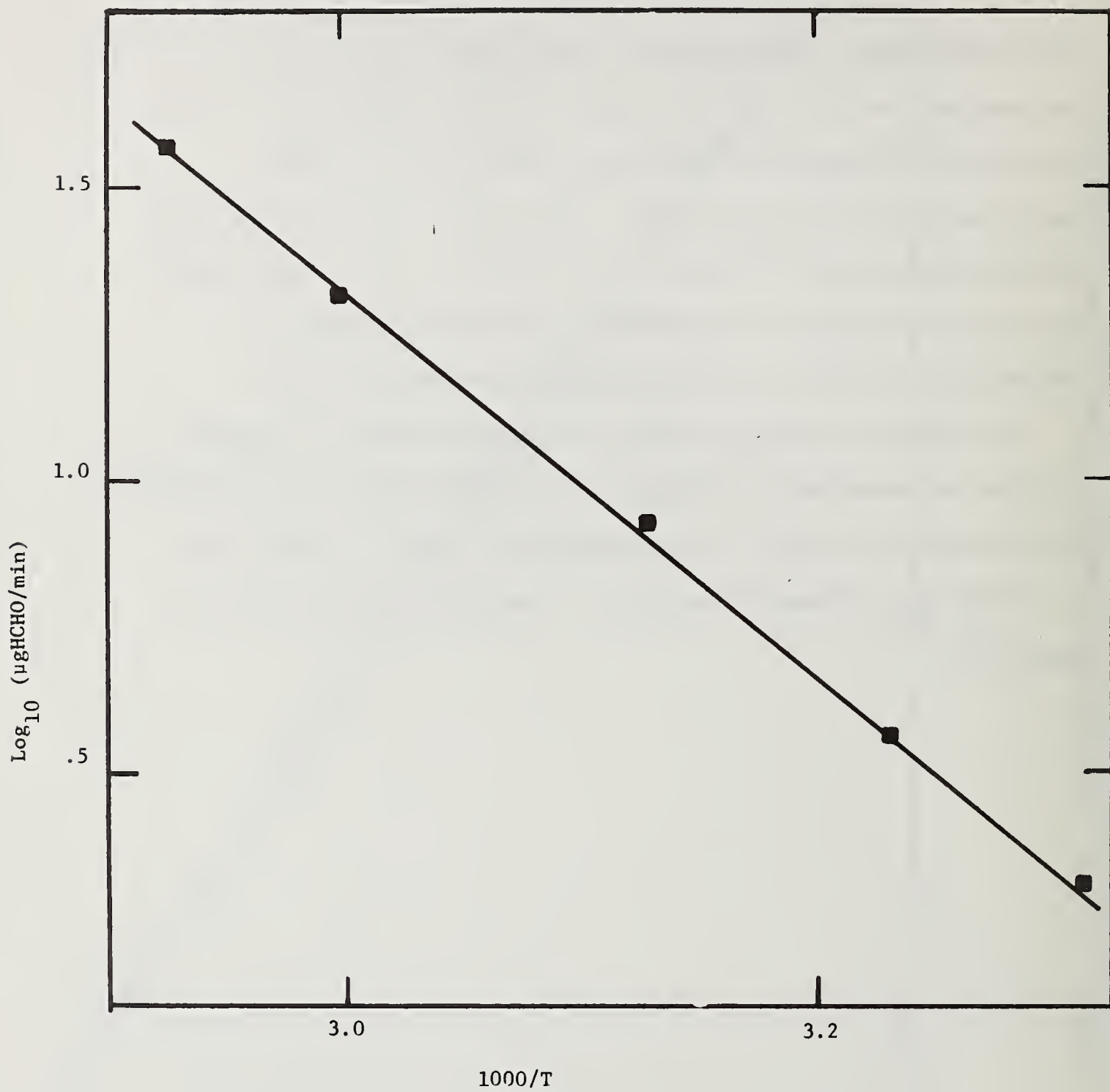in this system substantial quantities of methanol and water are also
generated.

FIGURE 11 Yields of HCHO/min from commercial formalin solution as a function

of temperature.

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Table I

a)   Long term behavior of formaldehyde generation. Cell temperature
40°C.   Flow rate = 30 cc/min.   Pyrolyzer at 650°C.   System pressure =
7.2 psig.

hours	concentration
0	75 ppm
2	75 ppm
6	74 ppm
72	76.5 ppm

b)   Variation of HCHO concentration as a function of flow rate at
88°C. 7.5 psig cell pressure. pyrolyzer temperature 675°C.

flow rate (cc/min)	(flow rate)$^{-1}$ (min/cc)	ppm HCHO
33.2	.0301	881
81.0	.0124	397
210.0	.0048	148

c)   Variation of HCHO concentration as a function of pressure at
88°C; 210 cc flow rate, pyrolyzer temperature at 655°C

pressure (psia)	ppm HCHO
26.4	122
22.1	148
18.3	172

Table II

Formaldehyde output from Reactive Gas Generator Using

Formalin Solution as 60.5°C.

time (hrs.)	flow rate	concentration (ppm)	mass thru-put (μg/min)
0	25 cc/min	678	20.9
66	25 cc/min	671	20.7
68	100 cc/min	167	20.5
70	200 cc/min	83.5	20.6

B) $\underline{CH_3CHO}$: The parent compound for acetaldehyde generation is 4-penten-2-ol. The decomposition reaction is
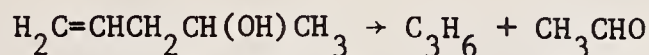
$$H_2C=CHCH_2CH(OH)CH_3 \rightarrow C_3H_6 + CH_3CHO$$

From gas chromatographic analysis with a Poropak P-S column and flame ionization detection the ratio of the areas of the propylene to acetaldehyde peaks is 2.89 $\pm$ .05 to 1. A plot of the results over a concentration range of a factor of 25 can be seen in Figure XII. When both substances are methanated the new ratio is 1.485 to 1. These ratios are sufficiently close to the expected 3 to 1 and 3 to 2 values so that the stochiometry can be considered to be established. Maximum thru-put (100% conversion) in terms of acetaldehyde output/min as a function of cell temperature can be found in Figure XIII. Least squares analysis of the data gives at 7.0 psig and over the temperature range of 30-90°C

$$Log_{10}[\mu g\ CH_3CHO/min] = 2814 \pm 30\ [\frac{1}{T}] + 9.86 \pm .09$$

The thru-put range is thus 4-100 µg/min. The standard deviation is of the order of $\pm$ 4%. Note that through the use of the internal standard a gain in accuracy of a factor of 2 is attainable. For flow rates of 20 to 100 cc/min (He) the pyrolyzer temperature setting for complete conversion must range from 650 to 700°C. The long term behavior of this system is summarized in Table III. In order to study the possibility of obtaining lower thru-put a hypodermic needle (0.025 in ID) has been epoxied into the horizontal portion of the 1/8 in diffusion column. The results as represented by the dotted line can be seen in Figure XIII. It is seen that thru-put has been lowered by a factor of 20. We did note however a substantial longer time period is required for equilibration.
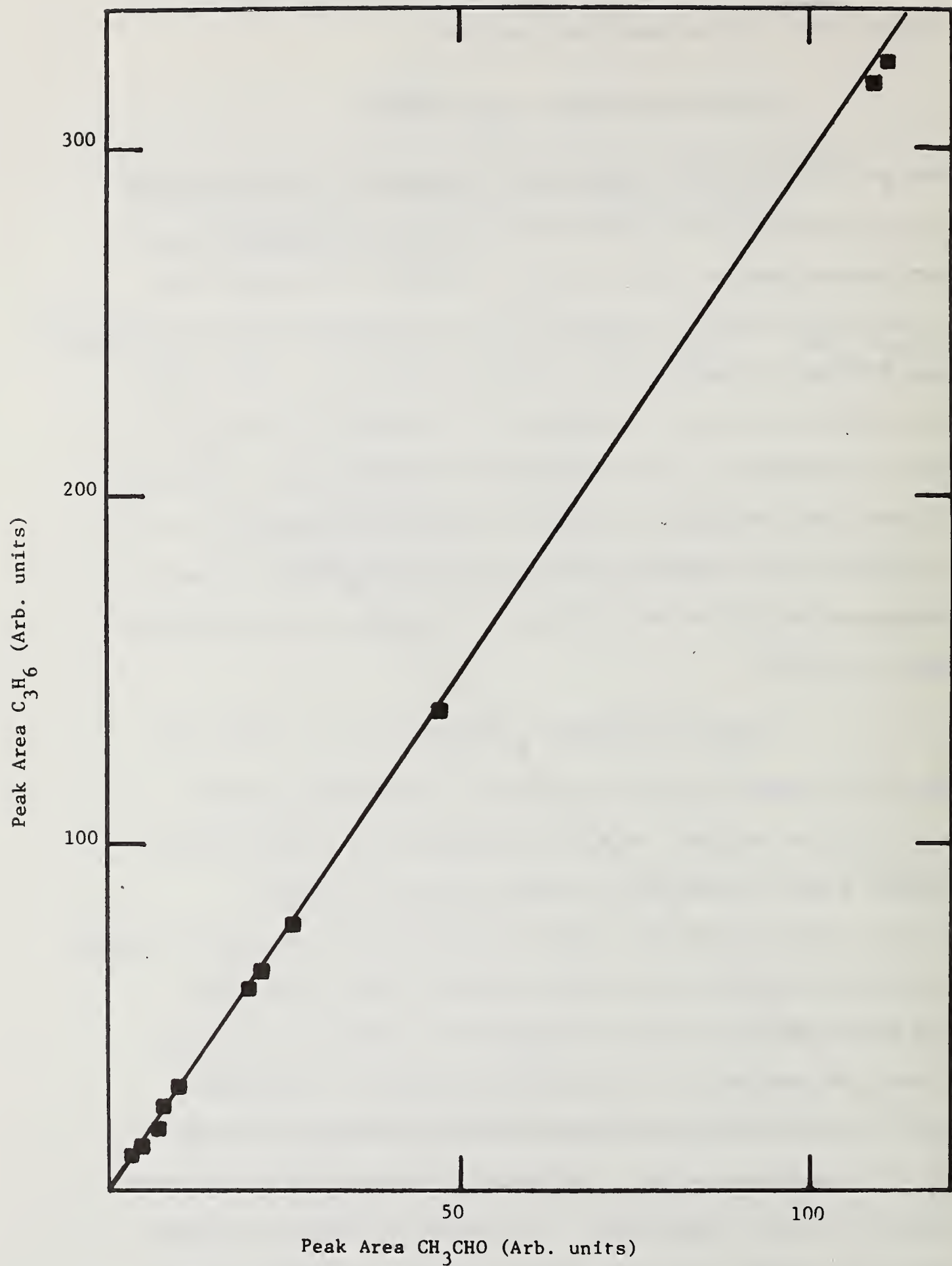
27

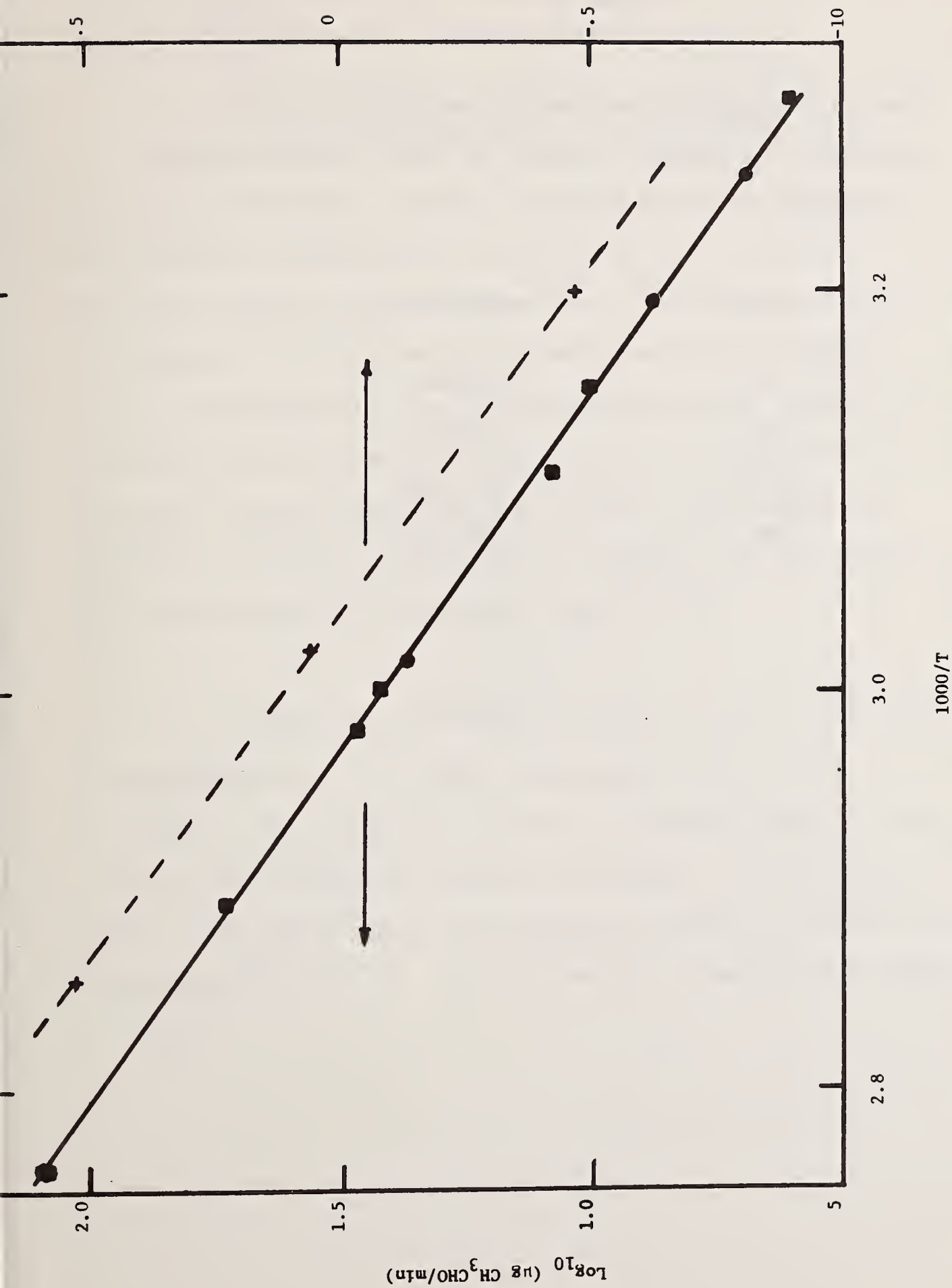FIGURE 12 Relative yields of propylene and acetaldehyde from 4-penten-2-ol.

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FIGURE 13 Yields of acetaldehyde/min from 4-penten-2-ol as a function of temperature. ■ and ● are from generators with 1/8 in diffusion column. + from generator with ~ 0.025 in diffusion column.
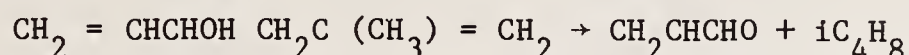
29

Table III

Long term behavior of acetaldehyde generator at 30.2°C.
Flow rate = 40 cc/min. Pyrolyzer at 680°C. System Pressure =
7.0 psig.

hours	concentration
0	56 ppm
96	58 ppm
120	58.5 ppm
168	56.5 ppm

C) CH_2CHCHO: The parent compound for acrolein generation is 5-methyl-1,5-hexadien-3-ol. The decomposition reaction is

$$CH_2 = CHCHOH \ CH_2C \ (CH_3) = CH_2 \rightarrow CH_2CHCHO + iC_4H_8$$

From gas chromatographic analysis with flame ionization detection the isobutene to acrolein ratio is $1.90 \pm .02$ to 1. In view of the earlier results with acetaldehyde this is sufficiently close to the expected 2 to 1 ratio and thus establishes the stochiometry. A plot of the results covering a concentration range of a factor of 30 can be found in Figure XIV. Maximum thru-put (100% conversion) in terms of acrolein output/min as a function of cell temperature is plotted in Figure XV. Least squares analysis of the data yields at 7.2 psig and over the temperature range of 30-90°C

$$Log_{10}[\mu g \ CH_2CHCHO/min] = 2901 \pm 27 \ [\ \frac{1}{T} \ ] + 9.49 \pm .08$$

The thru-put range is 1-30 μg/min. The standard deviation is $\pm 3.5\%$ and it should be noted that with the internal standard a gain of over a factor of two in accuracy is attainable. For flow rates of 20-200 cc/min (He) the pyrolyzer temperature setting for complete conversion must range from 600-675°C. Long term behavior is summarized in Table IV.

31
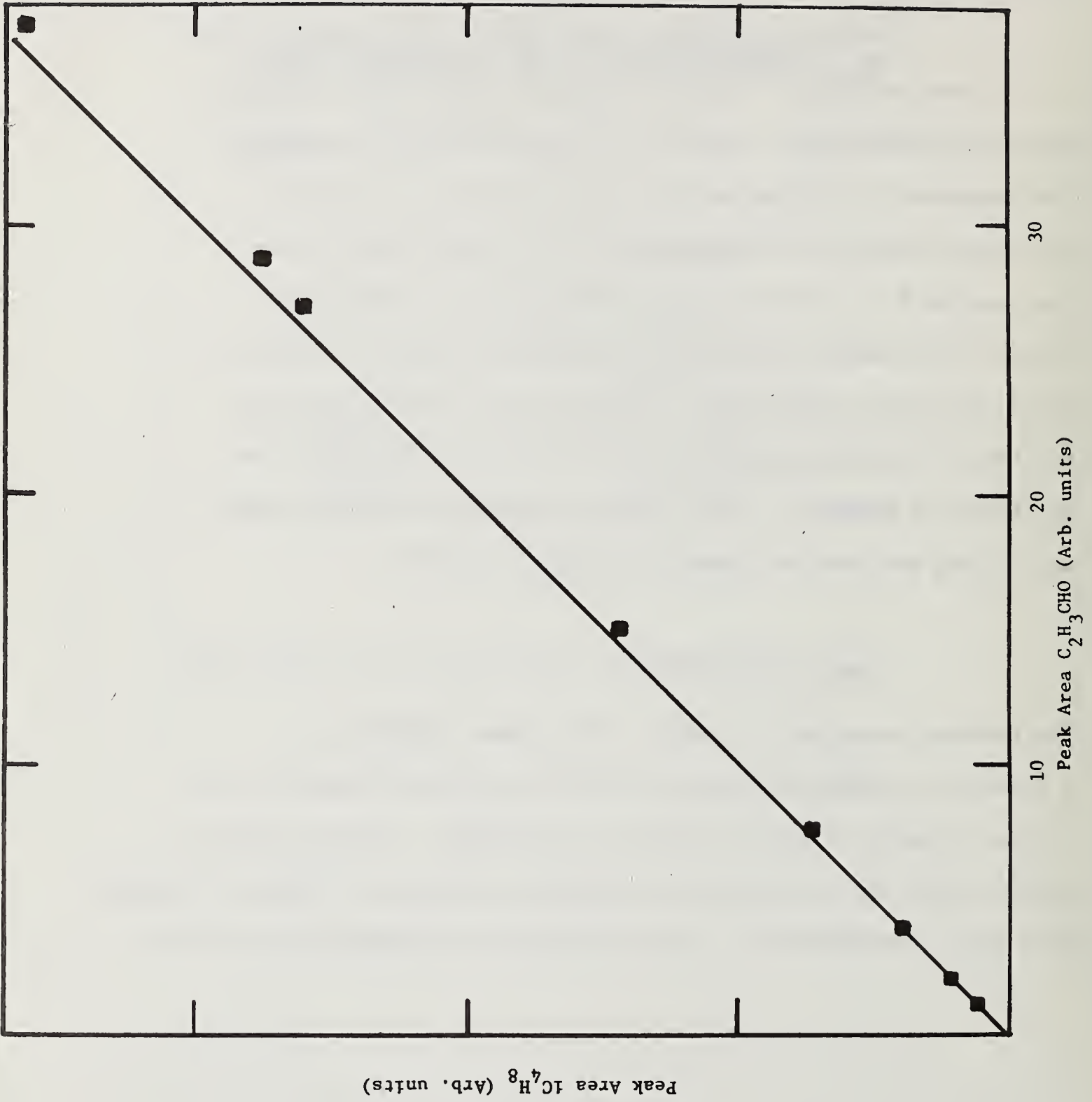
FIGURE 14 Relative yields of isobutene and acrolein from 5-methyl-1,5-hexadien-3-ol.
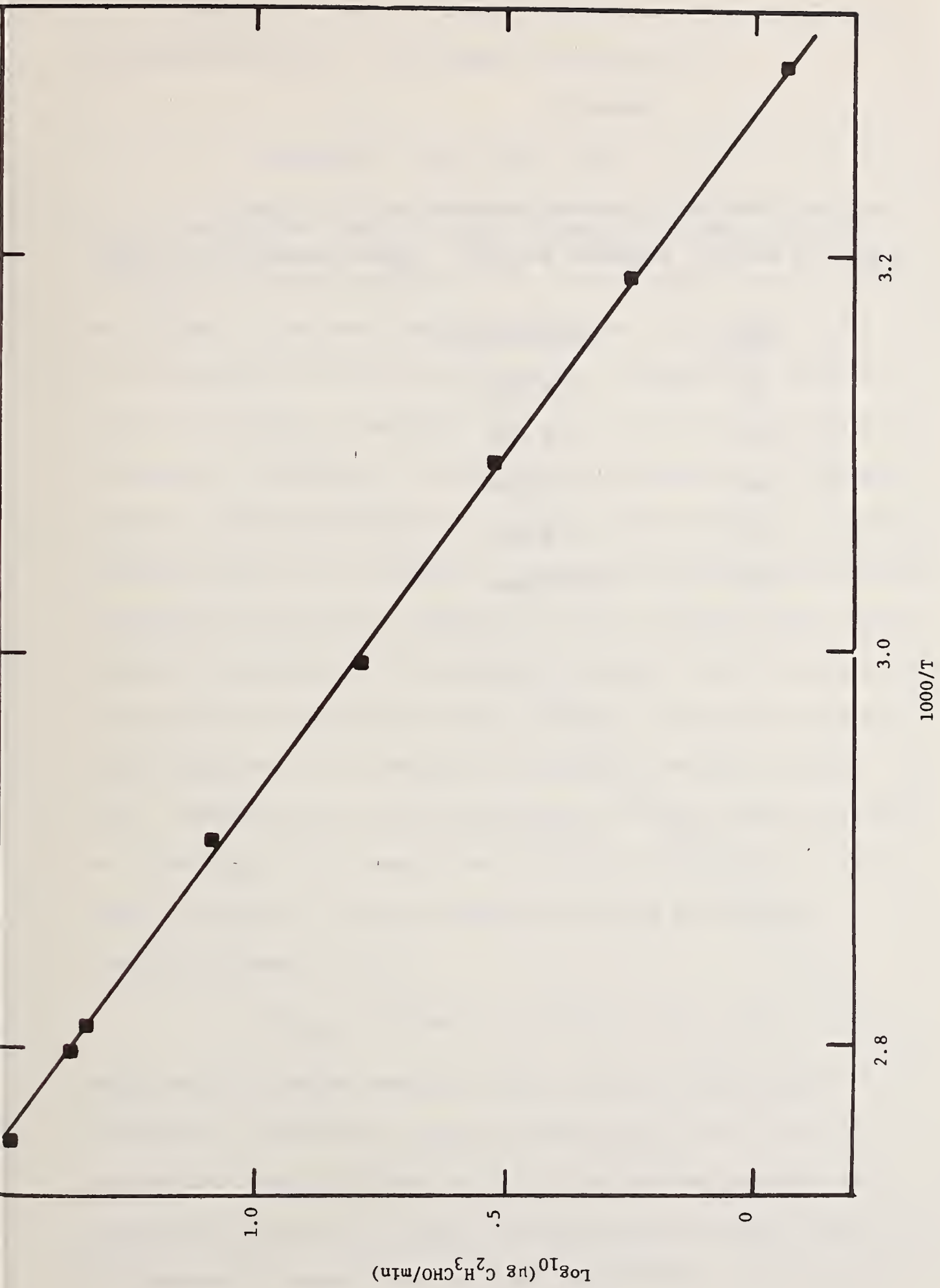
32

FIGURE 15 Yields of acrolein/min from 5-methyl-1,5-hexadien-3-ol as a function of temperature.

33

Table IV

Long term behavior of acrolein generator at 31°C. Flow rate = 40 cc/min. Pyrolyzer at 620°C. System pressure = 7.0 psig.

hours	concentration
0	9.7 ppm
24	9.6 ppm
48	9.7 ppm
72	9.8 ppm
96	10.0 ppm

D) <u>HCN</u>: The parent compound for hydrogen cyanide generation
is ethylcyanoformate. The decomposition reaction is

$$C_2H_5OCOCN \rightarrow C_2H_4 + HCN + CO_2$$
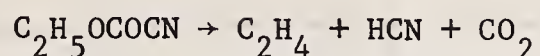
Gas chromatographic analysis with a Poropak P-S column and flame
ionization detection yielded over the entire range (a factor of 30)
an ethylene to hydrogen cyanide area ratio of 6.29 ± .09. A plot
of the results can be found in Figure XVI. Although the constancy
of the area ratio is suggestive, the lack of any literature values on
the relative sensitivity of flame ionization detections of hydrogen
cyanide to hydrocarbons prevents the use of this number to establish
the stochiometry of the reaction. Accordingly, absolute determinations
of HCN concentration have been carried out by collecting HCN in NaOH
solution and measuring CN^- concentration using a specific ion electrode.
The results are summarized in Table IV and it is seen that over the
entire range one to one production of ethylene and HCN is indeed the
case. Maximum thru-put (100% conversion) in terms of HCN output/min
as a function of cell temperature is plotted in Figure XVI. Least
squares analysis of the data yields at 8.8 psig and over the
temperature range of 30-95°C

$$Log_{10}[\mu g\ HCN/min] = -2316 \pm 29\ [\ \frac{1}{T}\ ] + 8.24 \pm .09$$

This covers a thru-put range of 4-100 µg/min and the standard
deviation or "settability" over this range is 4%. As is the case
for the two larger aldehydes the use of the internal standard will
improve the accuracy to ± 1.5%. For flow rates of 20-200 cc/min (He)
the temperature range of the pyrolyzer is 600-680°C. The long term
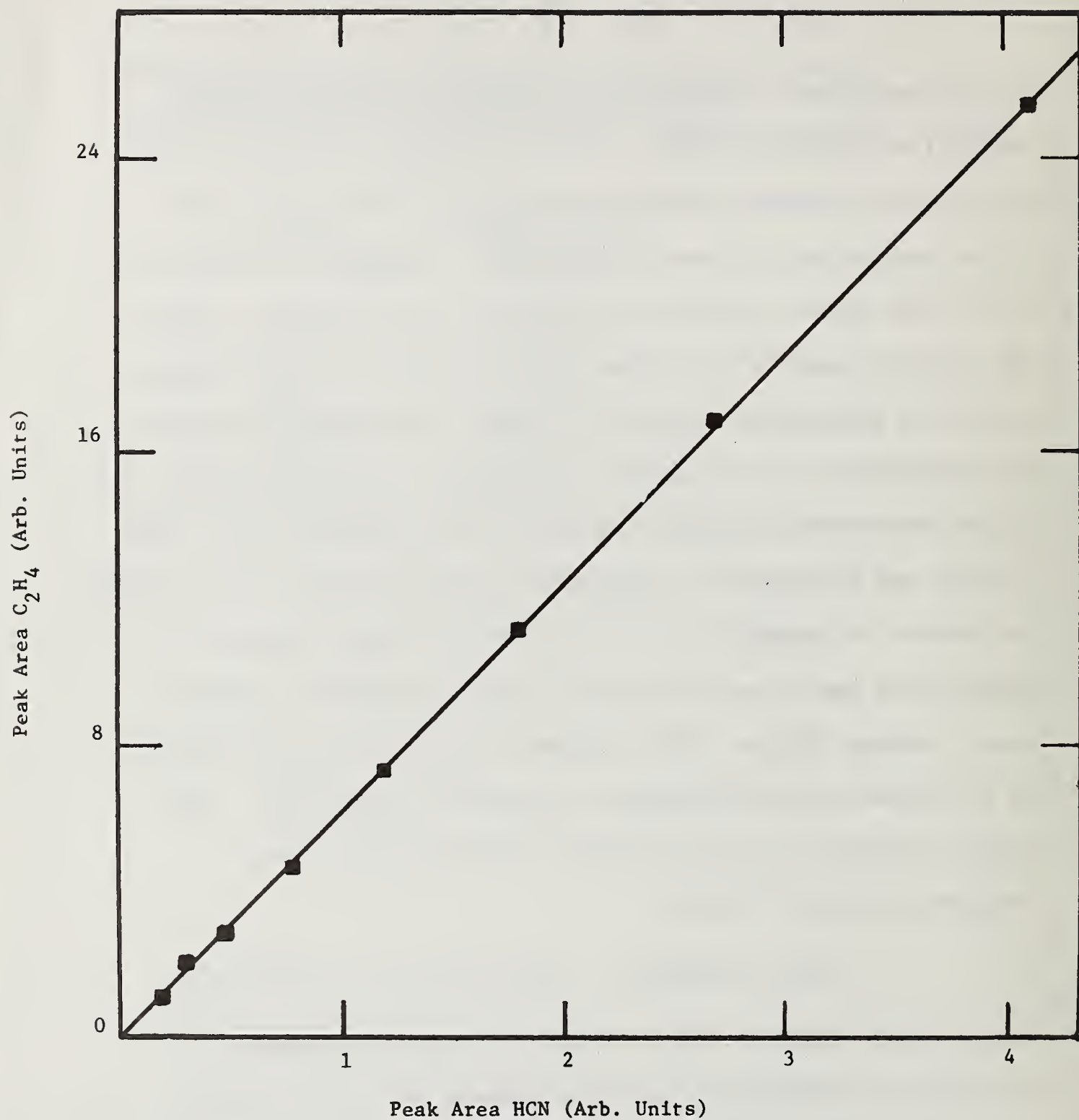behavior of the system is summarized on Table V.

FIGURE 16 Relative yields of ethylene and hydrogen cyanide from ethyl cyanoformate.

Table V

a) Comparison of ethylene and hydrogen cyanide yields from ethyl cyanoformate using G.C. and CN^- specific ion electrode.

Temp.	G.C. Analyses for Ethylene	Specific ion electrode analysis of CN^-
86°C	1440 ppm	1460 ppm
30°C	75 ppm	80 ppm

b) Long term behavior of HCN generator cell temperature 29.6°C
Flow rate ∿ 40 cc/min Pyrolyzer temperature = 630°C System Pressure = 8.8 psig.

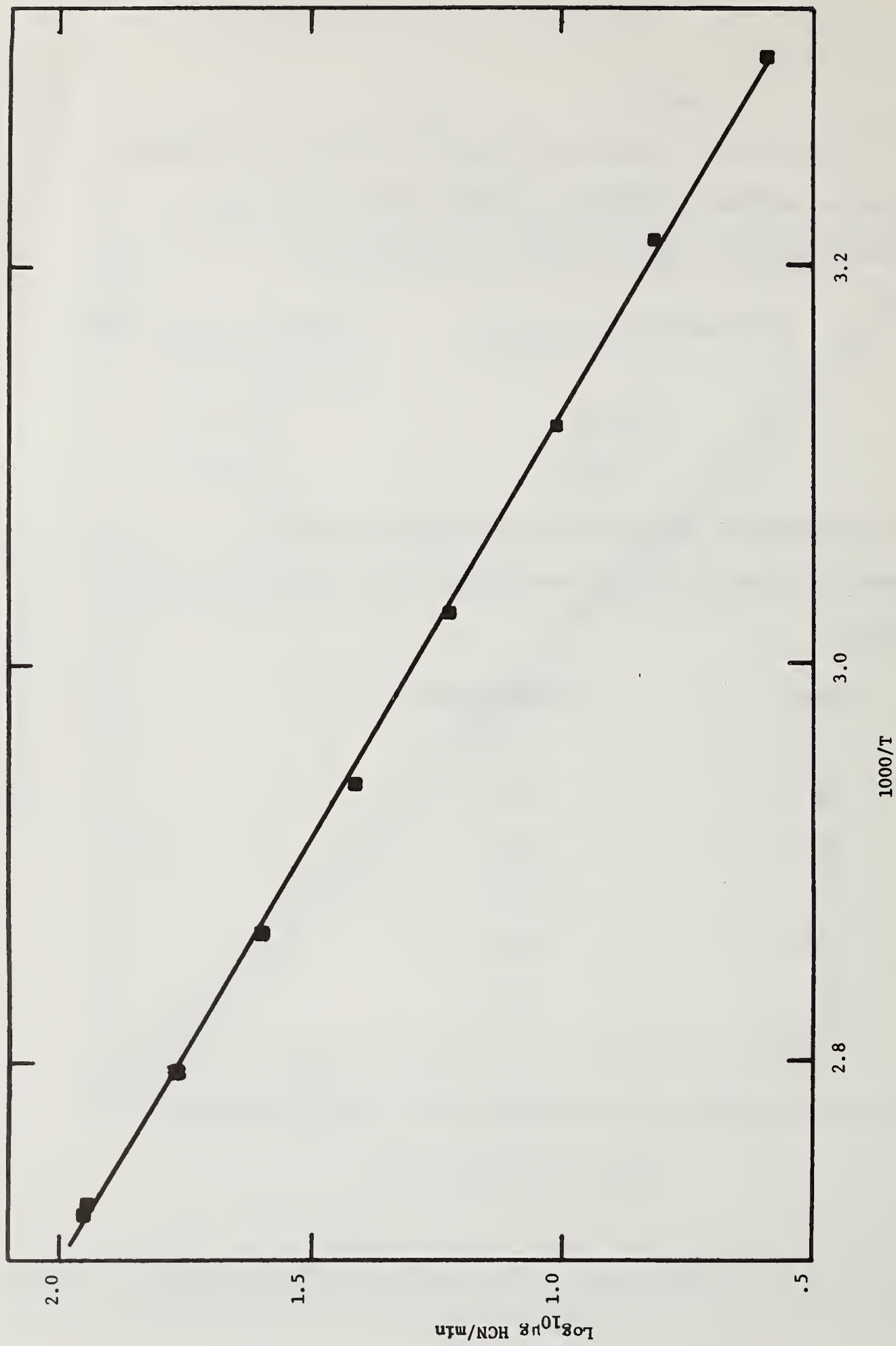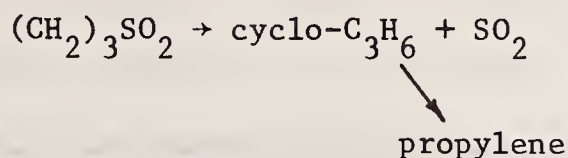| hours	thru-put μg/min
0	3.91
24	3.82
48	3.86
72	3.86
96	3.86
168	3.82

FIGURE 17 Yields of hydrogen cyanide/min from ethyl cyanoformate as a
function of temperature.

38

E) SO_2: The parent compound for sulfur dioxide generation is trimethylene sulfone. The decomposition reaction is

$$(CH_2)_3SO_2 \rightarrow cyclo-C_3H_6 + SO_2$$

$\searrow$

propylene

In an earlier report Cornell and Tsang (5), using an evaporative method (1) have demonstrated the utility of trimethylene sulfone as a source for SO_2. In particular, they show that in the range covered (10-100 ppm and 20-40 cc/min, flow rate) equivalent amounts of C_3 hydrocarbons and sulfur dioxide are produced. The present results will demonstrate that this compound is compatible with the new generator. Indeed, it is shown that the use of the diffusion technique offers a considerable increase in flexibility so that the range covered can easily be extended.

All of the present results have been obtained with a diffusion cell head containing a column with a 1/4 in diameter. This is in contrast to the 1/8 in diameter columns used for the other compounds. Gas chromatography with a Poropak T column and helium ionization detection is used for analysis. Because of an interfering water peak, which eluded on the tail of the SO_2 peak, the Poropak T column was preceeded by a methyl silicone column. Quantitation of the experimental results is based on bottled samples of propylene (206 ppm, measured) and sulfur dioxide (1000 ppm, stated). It is assummed that in the range covered the detector is linear. Total yield of C_3 hydrocarbons as a function of SO_2 yield is plotted in Figure XVIII. Over the entire thru-put range (a factor of 100) the ratio of hydrocarbon to SO_2 yield is $1.024 \pm .04$. Together with the earlier results this is a satisfactory demonstration of the
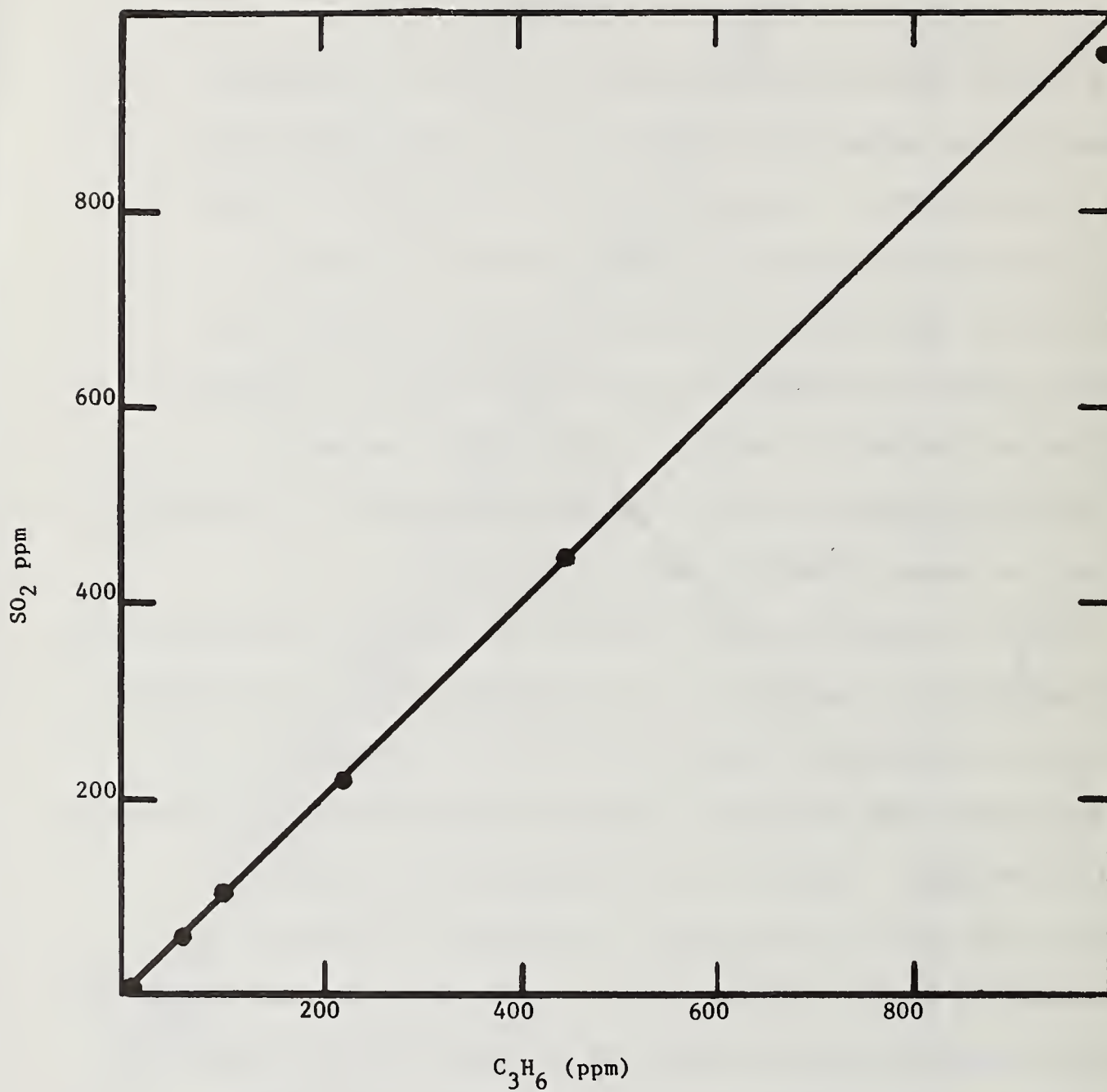
FIGURE 18 Yields of C_3 hydrocarbons and sulfur dioxide from trimethylene sulfone decomposition.

postulated stochiometry. The larger then usual uncertainty is

actually an artifact that arose from the existence of a small water

impurity which impinged on the tail of the sulfur dioxide peak.

This is especially important at low thru-put. Thus there is an

actual drift in the measured concentration ratio ranging from

.97 at thru-put of 100 µg/min to 1.09 at the 1 µg/min level.

It is suspected that the former number is more likely to be the

correct one and that had it been possible to correct for the

water peaks a lower uncertainty limit would have been obtained. We

have also attempted to measure sulfur dioxide concentration using

a sulfur dioxide specific ion electrode following the prescription given

by Orion Research. Unfortunately the results showed wide scatter

($\pm$ 50%) and have not been used. Maximum thru-put (100% conversion)

in terms of SO_2 output/min is plotted as a function of temperature

in Figure XIX. A least squares analysis of the data yields

$$\text{Log}_{10}[\mu g SO_2/min] = -3145 \pm 41 \left[\frac{1}{T}\right] + 9.16 \pm .1$$

The standard deviation is $\pm$ 5%. These data covers a thru-put range

of 1 to 100 µg/min and extends over the temperature range of 70-170°C.

Long term stability and the dependence of concentration on flow rate

is summarized on Table VI. For flow rates of 20-200 cc/min the pyrolyzer
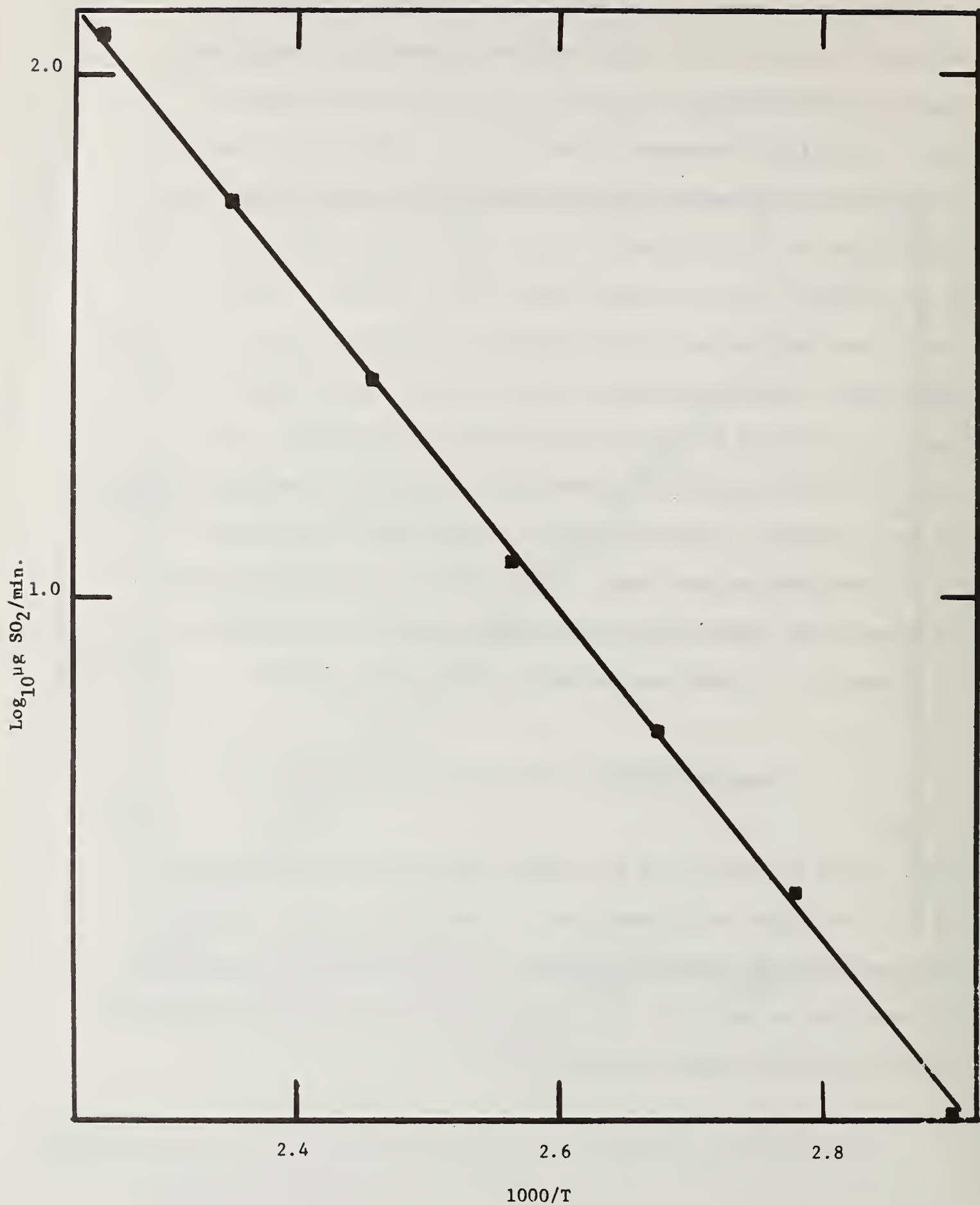
temperature should range from 600-660°C.

41

FIGURE 19 Yields of sulfur dioxide/min from trimethylene sulfone as a
function of temperature.

42

Table VI

a) Long term behavior of SO_2 generator Cell Temperature 100.5°C
    Pyrolyzer temperature ∿ 650°C Flow rate 41 cc/min.   System
    Pressure = 7.0 psig.

hours	concentration
0	58.6 ppm
3	57.0 ppm
6	57.2 ppm
24	57.8 ppm
27	56.8 ppm
31	57.0 ppm
98	57.8 ppm

b) Dependence of SO_2 concentration as a function of flow rate
    System Pressure = 7.0 psig Pyrolyzer temperature ∿ 650°C Cell
    Temperature = 100.5°C.

flow rate (cc/min)	concentration (ppm)
20.4	111.0
42.7	57.8
82.0	27.0
163.0	13.1

43

F) <u>HCl</u>: The parent compound for HCl generation is cyclohexyl chloride. The decomposition reaction is

$$C_6H_{11}Cl \rightarrow C_6H_{10} + HCl$$
$$\searrow$$
$$C_2H_4 + C_4H_6$$
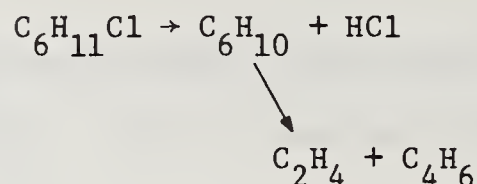
In the temperature range where these pyrolytic studies are carried out the conversion to ethylene and butadiene is less than 10%. Verification of the postulated stochiometry has been carried out using gas chromatography with a Porapak P-S column and flame ionization detection for the hydrocarbon and a Cl^- specific ion electrode for the quantitation of HCl yields. The results are summarized in Figure XX. The ratio of cyclohexene (including the small quantity converted to ethylene and butadiene) to HCl is $1.007 \pm .03$ to 1 and covers a concentration range of a factor of 25. Maximum thru-put in terms of HCl output per minute as a function of cell temperature can be found in Figure XXI. Least squares analysis of the data at 10 psig and over the temperature range 30-90°C yields

$$Log_{10}[\mu g \ HCL/min] = -2239 \pm 32 \ [\frac{1}{T}] + 7.81 \pm .09$$

In this temperature range the thru-put covers from 2 to 50 µg/min. The standard deviation is 4%. With flow rates in the 20-200 cc/min (He) range the pyrolyzer temperature must be set between 580-650°C. The long term behavior of the generator is summarized in Table VII.
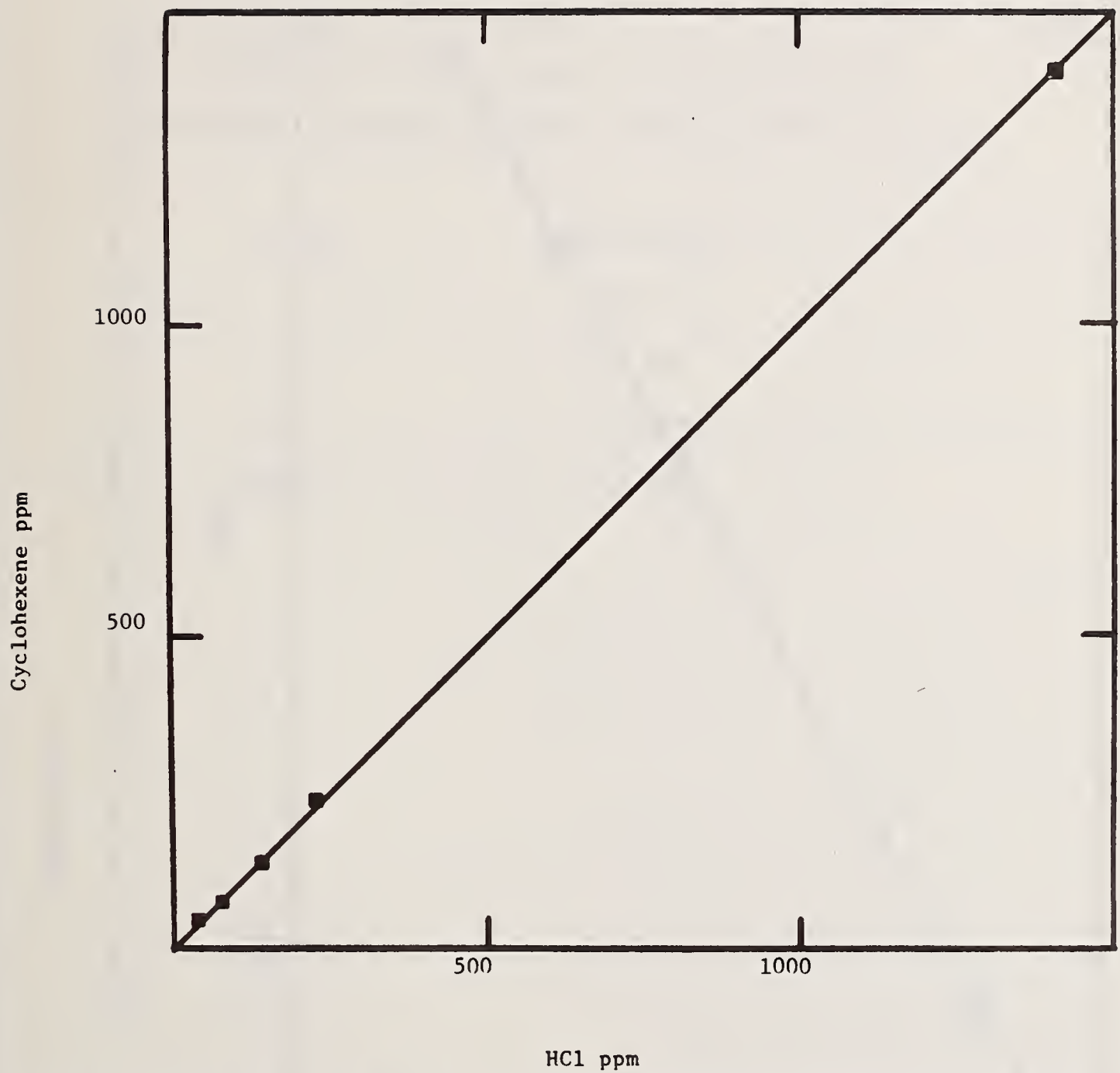
FIGURE 20 Yields of cyclohexene (including ethylene decomposition products) and butadiene, and HCl from cyclohexyl chloride.

FIGURE 21 Yields of HCl/min from cyclohexyl chloride as a function of temperature.

Table VII

Long term behavior of HCl generator at 49°C. Flow rate
∿ 40 cc/min. Pyrolyzer at 630°C.   System pressure = 10 psig.

hours	concentration
0	116 ppm
48	113 ppm
120	113 ppm
168	113 ppm

Parts List

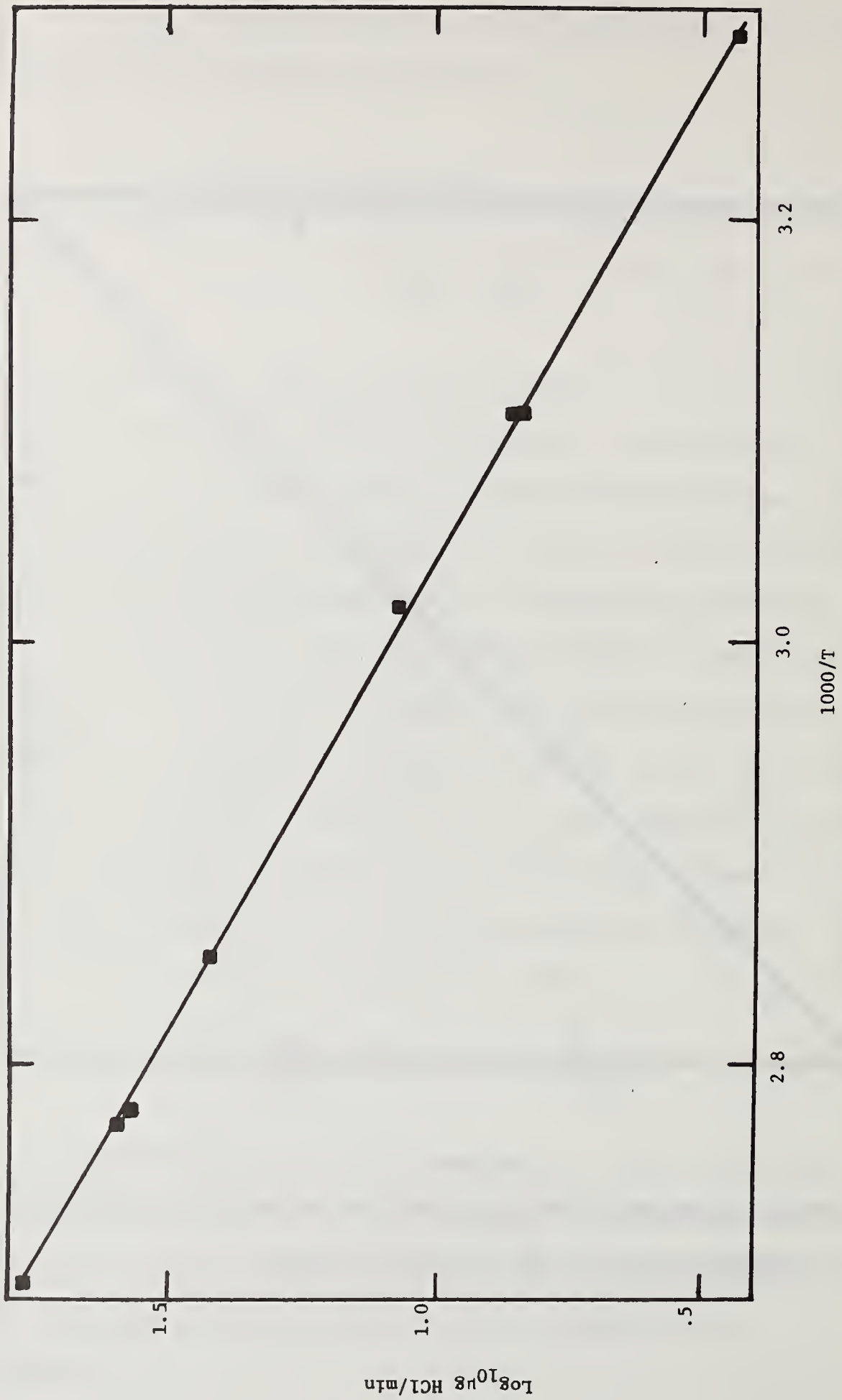|	
Cell Compartment Heater	4" x 10" flexible heater, 120 v 200 watts, cat. no. HF4-10 Thermal Corp., Huntsville, Alabama.
Furnace Heater	Firerod cartridge heater 5/8" dia. x 3" long 120 V, 500 watts. Cat. no. L3A113 Thermal Corp., Huntsville, Alabama.
Furnace Temp. Controller	Model A-1S Thermostat Burling Instrument Co., Chatham, NJ 07928
Cell Compartment Temp. Controller	RFL Model 870 Proportional Controller RFL Industries, Inc. Boonton, NJ 07005.

Valves

s.s. metering valve	s.s.-2mg NuPro	1 each
Brass Ball Valve	B41S2 (Whitney)	1 each

Swagelok Fittings

s.s. union 1/8" tube	s.s. 200-6	1 each
s.s. union 1/8" tube to 1/8" pipe	s.s. 200-1-2	2 each
1/8" tube to 1/8" pipe	B20-1-2	2 each
s.s. Bulkhead Union 1/8"	s.s. 200-61	1 each
s.s. Male Branch "Tee"	TTM	
Brass Bulk head union 1/8"	B-200-61	3 each

Tubing

s.s. 1/8" OD	10 ft.
copper 1/8" OD	1.5 ft.
gold .015" wall x .125" OD (.635 troy oz.)	1 ft.

SW1	Toggle switch	DPST
SW2, -3, -4	Toggle switches	SPST

Chemicals

3-methyl-3-buten-1-ol	Chemical Samples
4-penten-2-ol	Chemical Samples
5-methyl-1,5-hexadien-3-ol	Chemical Samples
ethyl cyanoformate	Aldrich Chemical Company
trimethylene sulfone	NBS
cyclohexyl chloride	Aldrich Chemical Company

References

1. G. O. Nelson, Controlled Test Atmospheres, Principles and Techniques Ann Arbor Science Publishers, Ann Arbor, Michigan (1971).

2. Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case dooes such identification imply recommendations or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment is necessarily the best available for the purpose.

3. S. W. Benson and H. E. O'Neal, Kinetic Data on Gas Phase Unimolecular Reactions, Nat. Stand. Ref. Data. Ser., Nat. Bur. of Stds. (U.S.), 21, 645 (Feb. 1970).

4. R. K. Stevens, A. E. O'Keefe and G. C. Ortman, unpublished results.

5. D. Cornell and W. Tsang, Analytical Chemistry, 933, 46, 1974.

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	14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

An instrument capable of generating a variety of reactive gases in trace levels has been constructed and tested. Operational details, with specific application to HCHO, CH$_3$CHO, CH$_2$CHCHO, SO$_2$, HCN and HCl production are discussed.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)* Acetaldehyde; acrolein; formaldehyde; gas chromatography; hydrogen chloride; hydrogen cyanide; pyrolysis; pollution; reactive gas generator; sulfur dioxide

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