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Research Study for

"Glass Shell Manufacturing in Space"

From September 6, 1979 to December 6, 1979

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ABSTRACT

Residual gases always found in glass shells are CO_2, O_2 and N_2. In those cases where high water vapor pressure is maintained in the furnace, water is also found in the shells. Other evidence for the existence of water in shells is the presence of water-induced surface weathering of the interior shell surface. Water and CO_2 are the predominant volatiles generated by the pyrolysis of both inorganic and hydrolyzed metal-organic gels. The pyrolysates of unhydrolyzed metal-organic gels also contain, in addition to water and CO_2, significant levels of organic volatiles, such as ethanol and some hydrocarbons; on complete oxidation, these produce CO_2 and water as well.

Water is most likely the initial blowing agent; it is produced copiously during the initial stages of heating. In the later stages, CO_2 becomes the dominant gas as H_2O is lost at increasing rates. Water in the shell arises mainly from gel dehydration, CO_2 by sodium bicarbonate/carbonate decomposition and carbon oxidation, and O_2 and N_2 by permeation of the ambient furnace air through the molten shell wall.

INTRODUCTION

This quarter we devoted most of our time to detailed reduction of data obtained over the past year. This report presents a summary and conclusion of the past year's effort.

As stated in our proposal "the ultimate goal of this research is to further the fundamental understanding of the physics and chemistry of the processes by which spherical glass shells are formed of the size, quality and economic quantity required by the inertial confinement fusion (ICF) program." This year's effort has concentrated on collecting data on the pyrolytic chemistry of the metal-organic gel when it is transformed into a Microshell® pellet. These experiments and analyses have led us to propose a couple of qualitative models of shell formation. These models will be discussed further in the plans for next year. We can test these models by removing or controlling some of the independent variables such as gravity, time at temperature, etc. Also, if levitations in a "one g" environment are not stable enough to allow transformation of a solid metal-organic gel particle into a hollow Microshell® pellet, a "micro-g" environment will be necessary to study the physical transformation.

OBJECTIVES

Such an understanding, from levitation in a "micro-g" environment, would facilitate the development of more general physical and chemical models, which could ultimately result in the control of and improvement on the shell processing parameters and shell quality. In the pursuit of these objectives, we have focused on several specific tasks:

a) collection and identification of the amount and composition of gases that form the shell (residual gases in shells),

b) determination of the amount and composition of gases generated by the gel during the shell-forming process,

c) determination of the temperature regimes of major chemical and physical transformations in the gel, especially those generating gases.

The progress made in these tasks is presented in this report.
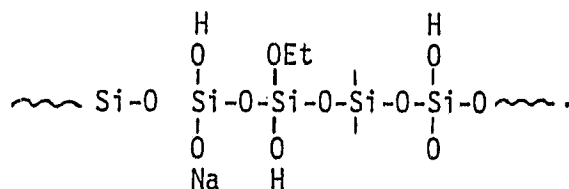
DISCUSSION OF RESULTS

Identification of Shell-Forming Gases

The model glass used in our study has the nominal composition, 80% by weight SiO_2 and 20% by weight Na_2O. The residual gases found in glass shells manufactured from gels of this oxide equivalent composition are CO_2, O_2 and N_2. The relative concentrations of these gases in five different shell samples, as determined by gas chromatography, are presented in Table 1. Carbon dioxide had been qualitatively confirmed earlier as a residual gas by mass spectroscopy. Other possible permanent gases, such as carbon monoxide or nitrogen oxides, were not detected by either gas chromatography or mass spectroscopy.
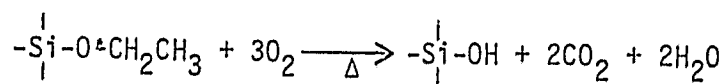
Carbon dioxide is the major gas constituent in the shells prepared from metal-organic gels. Oxygen and nitrogen are secondary, but together comprise 20 to 30% of the residual gases. Water does not appear in the gas analyses of Table 1, nevertheless, it is believed to be an important species in shell blowing. Indirect evidence for the existence of water vapor in the shell during the blowing process is the presence of "weathering" products detected on the interior surfaces of shells by scanning electron microscopy. These features are rich in sodium and nearly identical in appearance to those found on the exterior surfaces of shells and are commonly associated with any alkali-rich glass surface exposed to water vapor. It should also be noted that water has indeed been detected as a residual gas in two other glass systems when shells were prepared in a high water vapor environment. That water initially present in shells can be lost by reaction with the glass and/or diffusion through the shell walls was demonstrated in one of these other glass systems by repassing shells through the tower furnace. Water vapor, initially present at about 30% concentration, could not be detected in the residual gases of the repassed shells.
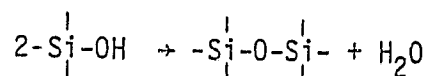
Blowing Agents and Their Sources

Carbon Dioxide. Based on its analogy to silica gel and its ˙.
synthesis chemistry, the metal-organic gel is presumed to be a polymeric
system, with an undetermined degree of 3-dimensional cross-linking.
Thermal gravimetric analysis (TGA) shows that the average-pristine-
vacuum dried gel contains about 15% by weight water and organic
volatiles. (See First Quarterly Report, 1979.) When pyrolyzed, the gels
produce substantial amounts of ethanol as measured by gas chromatography
(PGC). (See Third Quarterly Report, 1979.) From this information the gel
is believed to have a structure

$$
\begin{array}{c}
\overset{\displaystyle H}{\underset{\displaystyle Na}{\overset{\displaystyle O}{\underset{\displaystyle O}{}}}}\overset{\displaystyle OEt}{}\overset{\displaystyle H}{\underset{\displaystyle O}{\overset{\displaystyle O}{}}}
\end{array}
$$

∿∿ Si-O Si-O-Si-O-Si-O-Si-O ∿∿ .

(with H / O / OEt / O / Na / H and O substituents on the silicon chain)

Those ethoxide (OEt) moieties which are oxidized will potentially
generate four molecules of gas:

$$-\overset{|}{\underset{|}{Si}}-O\!\!-\!\!CH_2CH_3 + 3O_2 \xrightarrow{\Delta} -\overset{|}{\underset{|}{Si}}-OH + 2CO_2 + 2H_2O$$

and further

$$2-\overset{|}{\underset{|}{Si}}-OH \rightarrow -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + H_2O$$

This represents a copious source of blowing gas, i.e., there are four
and a half moles of blowing gas per mole of available ethoxide (OCH_2CH_3),
assuming a sufficiency of oxygen.

Since carbon dioxide is a major blowing gas, if its sole source
is oxidation of organic residues in the gel, then a reduction of
organic residues should affect shell formation. Such a reduction was
achieved by controlled hydrolysis of the gel. The extent of the

reduction in the gel was monitored by TGA, DTA, pyrolysis mass spectroscopy (PMS) and flash pyrolysis gas chromatography (PGC). Results using the first three techniques are described in detail in the Second Quarterly Report, but can be summarized by Figures 1 and 2. The anlayses of gel pyrolysis reaction products by gas chromatography are given in Table 2. The 10-month old samples were re-analyzed this quarter and confirm the initial results described in the Third Quarterly Report. The hydrolysis apparently succeeded in reducing the organic residues to almost zero except for traces of organics that produce CO and CH_4.

For comparison purposes a gel sample was prepared from an aqueous sodium silicate solution and also examined. In this case, there were no organic constituents used in the synthesis of the gel. The shell-forming experiments using unhydrolyzed metal-organic gel, hydrolyzed metal-organic gel and inorganic gel produced shells in surprisingly good quality and yield for all three gels. Some pertinent physical characteristics of the shells are shown in Table 3. Additional details are provided in the Third Quarterly Report, 1979. The residual gas analyses are shown in Table 1. The important result, summarized in Table 3, is that the inorganic gel, completely free of organic carbon, formed shells in significant yield. Further, metal-organic gels, freed substantially of organic carbon by hydrolysis, formed shells of uniformity and size similar to those formed from organic-rich gel although the aspect ratio of the former is lower. These results conflict with those expected from a comparison simply of the potential organic volatiles of these gels, as summarized in Table 2, and suggest that CO_2 from oxidation of organic species may not be the dominant factor in forming shells from metal-organic gels.

The flash PGC data and the shell-blowing experiments for gels wherein the organic content was substantially eliminated require that the source of CO_2 in these gels, and their resultant shells be either inorganic sources, oxidation of trace organics or both. The fact that shells can be formed from inorganic gel indicates that trace organics in hydrolyzed metal-organic gels are playing only a partial role, if any.

Inorganic sources of CO_2 are sodium carbonate or bicarbonate. Adsorbed or trapped air will not supply enough CO_2 to blow shells since the natural level of CO_2 in air is only 0.033%. A CO_2 concentration mechanism is required, and can exist in the form of the reactive alkali (sodium) in the gel. Sodium bicarbonate, $NaHCO_3$, which forms on exposure of NaOH to CO_2 should release CO_2 over two distinct temperature ranges: a) 100 to 300°C, with generation of CO_2 and H_2O by decompositions of $NaHCO_3$ to Na_2CO_3, and b) above $\sim$ 900°C, with generation of CO_2 by carbonate decomposition. To test for this mechanism, experiments were conducted with gels in which the carbonate/bicarbonate was both minimized and maximized. The difference in CO_2 content of the gels, as monitored by flash PGC, was, where possible compared to shell-blowing results to assess the source and the role of CO_2.

First, attempt was made to minimize the carbonate content of the gel by synthesizing and maintaining the gel under argon, free of air, water vapor and ambient CO_2. A portion of the same argon-processed gel was then also hydrolyzed under argon to remove, as much as possible, all organic carbon. This latter sample should not be able to generate significant levels of CO_2, either by carbonate decomposition or oxidation or organics. Flash pyrolysis gas chromatography analyses for volatile content in these gels are summarized in Table 4. Note that there is a significant reduction, but not total elimination, of CO_2 due to processing the gel under argon instead of ambient air. (Cf. C and D of Table 2.) Residual CO_2 and residual organics still exist in the hydrolyzed sample (B) as well. The two gel samples formed shells in roughly comparable yields of similar quality and comparable aspect ratio to those of air processed gels as can be seen by a comparison of shell properties in Tables 3 and 4. In addition, residual gas analyses of the shells (Table 1) indicate a preponderance of CO_2 in all samples; gas analyses are essentially the same, whether the gel is carbonate-deficient or not. A more complete discussion of pyrolysis studies of gels made and hydrolyzed under argon and shells blown from them is given in the Third Quarterly Progress Report, 1979. The results show that, in essence, minimizing the carbonate levels (and the organic residues as well) has no significant effect on CO_2 levels in the shells.

The effects of maximizing the carbonate levels in gels were also examined. This study was carried out using gel that had been synthesized and stored under argon. Pyrolysis GC results are reported in Table 5. An unhydrolyzed sample (A) was kept under pure argon and then exposed to CO_2 (A'). No physical changes could be seen, but subsequent pyrolysis GC indicated a substantial increase in CO_2 generation by the gel. When the argon stored gel was hydrolyzed under argon (B) no noticeable change in surface features occurred until subsequent exposure to CO_2 (B'). A very crystalline mat formed on the gel particles which was quite easily removed by the abrasive action of resieving (B"). It is quite apparent that the carbon dioxide reacting with the gel exists primarily in an abradable surface product, presumably sodium carbonates. If hydrolysis and carbon dioxide exposure are done simultaneously, sample B'", by placing the gel in a sealed vessel containing water and 100% CO_2, a crust also forms on the gel particles, but is less dramatic. Energy dispersive x-ray spectroscopy (EDXS) showed that the surface features on the gels exposed to high concentrations of CO_2 were very sodium rich and that pits on the gel surface left by spalling of the crystalline surface features were sodium poor and silicon rich. Shell blowing experiments with the last gel sample, B'", gave very poor quality, very thick-walled shells which appear not to have blown out. The glass in the shells appeared inhomogeneous when viewed with an optical microscope. Obviously, the rapid formation of carbonate produces a poor starting material for shell production.

These experiments indicated that neither;

a) reduction of organic residues in the gel,

b) reduction of carbonates, nor

c) reduction of both CO_2 sources,

significantly affected the formation and the quality of shells, nor the anlaysis of residual gases in shells. This implies that the source of the blowing gas CO_2 needs to be present in gels in only minute quantities. The concentration of CO_2 in the gel, in the form of carbonates, was calculated from TGA and PGC analyses. A comparison of

this value with the calculated concentration of CO_2 in the residual gas of the corresponding shells showed that, even for the worst case gel, such as gel B, more than enough carbonates, or organic residues, were present in the gel to drive the shell expansion.

Oxygen and Nitrogen. In addition to carbon dioxide, oxygen and nitrogen comprise the residual gas in the shells as shown in Table 1. Significantly, the oxygen is found in anomolously <u>high</u> levels compared to nitrogen; whereas in air $O_2/N_2 \approx 0.27$, in shells it is often $O_2/N_2 > 1$.

The high O_2 levels suggest that O_2 and N_2 permeate through the molten shell wall, but at unequal rates, and are not the result of air encapsulation caused by gel sintering. A further argument against encapsulation of ambient gases, such as air, in the gel during shell blowing is the observation that shells from gel made and stored under argon, but blown in an air-filled furnace, contained air, but no argon. The presence of argon is readily detectable by mass spectroscopy. Finally, the higher than expected O_2 levels are not the result of H_2O thermolysis, as an increase of the water vapor pressure in the furnace does not increase the O_2/N_2 ratio. (See the following section.)

A further confirmation that permeation of ambient gases can occur during or after shell formation was shown in a shell-blowing experiment using a partial backfill of argon in the furnace. A small amount of argon ($\sim 5\%$) was found in the shells. Shells of another composition, taken from KMSF stock, were repassed through the furnace partially filled with argon. The resulting shells had similar argon levels as the above shells made in argon, and in this case argon could only be present by diffusion through the shell wall.

The role of ambient gases in shell blowing has not been determined. However, it is likely that such inpermeation can help retain the molten shell size and may even increase it.

Water. Water is the largest component of volatiles generated by thermolysis of the gels. Considerable quantities are detectable in staged PGC (and PMS) throughout the whole temperature cycle. Although half of the potential H_2O is generated at low temperature, up to 200 or $300^\circ C$, the balance is generated continuously and in fairly constant
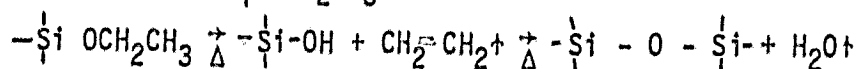
quantities throughout higher temperatures. Figure 3 shows this pattern for several gels.

The sources of the water are several: a) physically adsorbed and absorbed molecular water, b) thermolysis of Si-OH (produced by hydrolysis of Si-OEt),
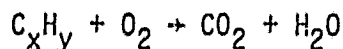
$$2 - \overset{|}{\underset{|}{Si}} - OH \overset{\Delta}{\rightarrow} -\overset{|}{\underset{|}{Si}} - O - \overset{|}{\underset{|}{Si}} - + H_2O \uparrow$$
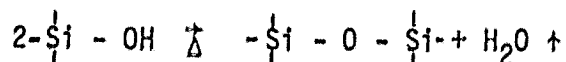
c) decomposition of $NaHCO_3$ $\quad 2\ NaHCO_3 \overset{\Delta}{\rightarrow} Na_2CO_3 + CO_2 + H_2O$

d) thermolysis of $-\overset{|}{\underset{|}{Si}}OCH_2CH_3$

$$-\overset{|}{\underset{|}{Si}}\ OCH_2CH_3 \overset{\rightarrow}{\Delta}\ -\overset{|}{\underset{|}{Si}}-OH + CH_2\overset{=}{=}CH_2\uparrow \overset{\rightarrow}{\Delta}\ -\overset{|}{\underset{|}{Si}} - O - \overset{|}{\underset{|}{Si}} - + H_2O\uparrow$$

e) oxidation of organic residues

$$C_xH_y + O_2 \rightarrow CO_2 + H_2O$$

All of these are likely sources; while the first three are probably predominant, we have not yet attempted to quantify or prove these mechanisms.

Water in the gel is of significance, in that it may serve as an initial blowing agent and modify the final glass viscosity. The water present in the inorganic gel and in the "CO_2-free", hydrolyzed metal-organic gel may be the reason that these formed shells readily. Possibly it is because of the H_2O content in these gels that changes in CO_2 and organic residue content seem to have less than the expected effect on the consequent shell formation, in yield or in quantity.

Observation of gel changes during heating with a hot stage microscope, conducted this quarter, yielded some insight on this. The inorganic gel, basically a water-glass, formed a hollow, fairly uniform spheroid at 300°C that was surprisingly thin-walled (AR ∿ 15-20) and transparent. The hydrolyzed metal-organic gel, with a comparable composition and surface area (indicating no porosity), formed spheroids as well between 200 to 300°C, although not as uniform nor as transparent. These spheroids, however, were more stable and did not collapse as readily during heating to melt, indicating a non-permeable gas content

(CO_2) that maintained the shell shape as the water diffused out. The unhydrolyzed metal-organic gel, with considerable surface area (and presumably porosity) did not spheridize; it did, however, undergo foaming and some slight expansion (pop-corn effect) about $400^{\circ}C$. These results imply that even though much of the volatiles generated at low temperature are lost through the pore structure, initial void formation occurs early in the gel, and may be driven by water vaporization.

In addition, increasing the water vapor in the furnace to retard the loss of H_2O by the gel, has resulted in significant water vapor pressure in the residual gas of shells as blown. The permeation of water in and out of shells has also been demonstrated by the repass of shells in the furnace in the presence and absence of high water vapor concentrations. The results of these experiments are summarized in Table 6. These results indicate that water may be only the initial, but an active agent, and may permeate rapidly out of the molten shell when the water vapor pressure in the furnace is low. Weathering of the internal surfaces observed in some shells further implies that significant water vapor levels may exist in shells during formation.

Gel Morphology Changes With Temperature

To understand the shell-forming mechanism, a correlation of the changes in physical gel morphology with gel thermolytic chemistry is required. Such a correlation is difficult to develop and a definitive one has not yet been achieved. In this work, we have used several thermal analytical techniques such as TGA, PGC and hot stage microscopy to crudely model the shell-blowing process and to analyze the physical changes and chemical products from that process. The heat transfer rates of these techniques, unfortunately, are quite slow compared to those expected in the real shell-forming process. With the analytical techniques described, the gel responds more uniformly to temperature changes and the resulting volatiles have ample time to escape from

the gel bulk by diffusion. In contrast to this, the rapid heating
rates achieved by dropping gel into the vertical furnace can be expected
to trap more volatiles in the gel. These differences in heating rates
undoubtedly cause other effects, but differences in gas evolution
rates is one of the most certain. Nevertheless, observations of
physical changes in the gel by hot stage microscopy can be of some
value in developing an over-all model of shell formation. Some of the
changes in gel morphology that can be seen when the sodium silicate gels,
used most extensively in this study, are heated in a microscope hot
stage are categorized in Figure 4. The gel prepared from inorganic
sodium silicate, E, forms a spheroid at $150^\circ C$ which has the appearance
of a crude shell at $300^\circ C$. The hydrolyzed metal-organic gel sample (B),
which like the inorganic silicate sample has a very low surface area
(< 0.1 m^2/gm), also produces a spheroid at relatively low temperatures
(250 to $400^\circ C$), but a crude hollow shell does not form until about
800 to $900^\circ C$. The unhydrolyzed gel, A, which is organic rich,
water-poor and has a high surface area (~ 300 m^2/gm) compared to
the other samples, remains rigid until about $500^\circ C$, but sporadic
movement of the gel particles testifies to some gas evolution. At
about $500^\circ C$ some foaming and expansion occurs and carbonization is
seen. A spheroid, probably solid, is finally formed at about 800
to $900^\circ C$. Other, more complex glass systems, behave most like sample
A when examined by hot stage microscopy. In general, the metal-organic
gels remain rigid and unchanged until 500 to $600^\circ C$, when carbonization
takes place, i.e., when residual organic species undergo non-oxidative
decomposition. Gels containing organic residues further undergo a
volume increase due to foaming, much like pop-corn, followed by
glass flow at the surface at 600 to $700^\circ C$. Melting of the "glass"
and oxidation of carbon occurs at 800 to $1000^\circ C$. The oxidation of
the trapped carbon probably provides a significant quantity of CO_2
for driving the shell expansion to completion in this temperature
regime. Fully hydrolyzed gels undergo foaming at $400^\circ C$, which implies
that the pore structure of the gel is closed at the gel surface;

otherwise, they are the same as described above. On the basis of observations made during many shell-blowing experiments over several years and hot stage microscopy studies such as those just described, a general gel morphology change with temperature model is proposed, as outlined in Figure 5. The important stages are;

    a) gel surface sintering,

    b) particle spheridization,

    c) internal void coalescence, and

    d) void expansion.

The model is a general one, and the characteristic temperatures of each stage may vary substantially, depending on the nature of the gel.

CONCLUSIONS

Experimental work this quarter involved additional shell residual gas analyses, repeat of some earlier pyrolysis gas chromatography on gels, and hot stage microscopy of inorganic and metal-organic sodium silicate gels. Considerable time was also devoted to a review of the results of the previous three quarters. Combining our results to date, the following conclusions can be made:

1. Carbon dioxide is the principal gas in shells formed from metal-organic gels. Gel pyrolysis experiments using thermal analytical, mass spectrographic, and gas chromatographic techniques have shown that CO_2 can arise from oxidation of organic or decomposition of inorganic (carbonate/bicarbonate) sources. When only inorganic sources of CO_2 are available, such as in gels made from aqueous sodium silicate solution, the resultant shells have low aspect ratios and the amount of CO_2 in the residual gases is low. The relative concentration of inorganic or organic CO_2 sources in metal-organic gels is determined by the degree of exposure of the gel to water vapor and CO_2. Dry conditions maximize organic sources and minimize inorganic while humid ambient air exposure produces the converse. The influence these conditions have on the course of the shell-formation process is complicated by the action of water on the gel. Nevertheless, the amount of CO_2 in the shell is not greatly affected. Apparently some compensating processes occur to generate similar effective amounts of CO_2 whether the gel is hydrolyzed or not.

2. Oxygen and nitrogen are present in the residual gases presumably as a result of permeation. They are not observed in pyrolysis of gels. Oxygen to nitrogen ratios higher than those found in ambient air can only reasonably be accounted for by a much faster rate of diffusion of oxygen compared to nitrogen. The identification of argon in shells repassed into an argon-filled furnace further supports the concept of diffusion of ambient gases into and from shells.

3. The importance of water in the gel and in the tower furnace has been
    demonstrated by a combination of observations. Water is the major
    product of gel pyrolysis (unhydrolyzed gel kept under argon is an
    exception). Glasses which are susceptible to weathering, especially
    high alkali glasses, generally show surface features on the interior
    shell walls. These features are attributed to reaction of trapped
    water vapor with the glass during shell cooling. When shells were
    blown in the tower furnace having a high concentration of water
    vapor, about 30% of the gas in the shells was water with interior
    surface features greatly enlarged. Upon repassing these shells into
    the furance filled with dry air, all water was removed from the
    residual gases. This confirms the ease of water diffusion through
    the glass shell wall at shell-forming temperatures. Hot stage
    microscopy showed that water-rich gels form glassy phases at low
    temperatures (< 300$^{\mathrm{o}}$C). Water deficient gels foamed at $\sim$ 500$^{\mathrm{o}}$C
    implying that gels with different water content may have different
    optimum processing temperatures.

EXPERIMENTAL

During the course of this project, a variety of techniques and instruments was used for synthesis and analysis of gels and shells. A large portion of these has already been described in the three previous quarterly reports. All of the techniqeus are summarized here in the form of a listing; those that have not been previously covered are described subsequently.

Synthesis Procedures
1. Gel synthesis was described in the first quarterly report.
2. Gel aging, accelerated by exposure to constant humidity in an
   a) air environment - described in the first report;
   b) argon environment - described in the third report.
3. Shell formation, using a drop tower furnace, was described in the second report.

Gel Analyses
1. Thermogravimetric analysis (TGA) - described in the first report; see Figure 6.
2. Differential thermal analysis (DTA) - described in the first report; see Figure 7.
3. Pyrolysis - mass spectrometry (PMS) - described in the second report.
4. Pyrolysis - gas chromatography (PGC) - described in the second report; see Figures 8 and 9.
5. Atomic Absorption analysis (AA) - described in the second report.
6. Scanning Electron Microscopy and Energy Dispersive Spectroscopy (SEM/EDS) - described in the second report.
7. Particle sizing - described in the second report.
8. Surface area - attached.
9. Hot stage microscopy - attached.
10. Differential Scanning Calorimetry (DSC) - attached.

Shell Analyses
1. SEM/EDS
2. AA
3. Photomicroscopy - described in second report.
4. Microradiography - attached.
5. Interferometry - attached.
6. Residual gas analysis - attached.
7. Residual gas pressure analysis - attached

Analytical Techniques Not Previously Described

Residual Gas Analysis by Gas Chromatography. The residual gases
in glass shells were analyzed by gas chromatography. The analytical
system consisted of a Varian 1420 dual-column, thermal conductivity
gas chromatograph, a Spectra Physics Autolab System IV recording
integrator and a Varian A-25 strip chart recorder. A chromatography
column (Alltech Associates, Model CTR, Cat. No. 8700) which can resolve
O_2 from N_2 was used at $25^{\circ}C$ to analyze the gas mixture; the detector
was maintined at 250 ma and column flow at 60 ml/min helium for maximum
sensitivity and resolution. A Porapak N column (Alltech 2716 PC)
was used to analyze for water in the residual gas; the column was
maintained at $120^{\circ}C$, and the detector at 150 ma. Detector response
was calibrated using known quantities of a standard gas mixture (Alltech
Cat. No. 9800) and injections of water-methanol solutions. The shell
crusher, adapted from a Whitey 4PDF4 stainless steel plug valve, was
attached directly to the column inlet, as shown in Figure 10.

Hot Stage Microscopy. The hot stage microscope, shown in Figure 11,
consists of a Leitz-Wetzlar heating stage, model 301-200 401, mounted
under a Bausch and Lomb Stereozoom microscope. The gel sample was
held in a platimum crucible, which in turn was heated by platimum
ribbon strip heaters. The maximum sample temperature was limited to
$1200^{\circ}C$. Heating control was entirely manual, thus the heating rate was
not controllable nor reproducible. The normal cycle time for heating
the gel sample was 15 minutes. The sample was heated under an air stream.

Surface Area Analysis. The specific surface area of gels was determined by the B.E.T. method using a Monosorb Surface Area Analyzer, an instrument made by Quantachróme, shown in Figure 12. Samples were degassed by heating at 120°C for 2 to 4 hours prior to testing. The surface area was obtained from a single-point determination using a gas mixture of 30% N_2 in helium.

Differential Scanning Calorimetry (DSC). A DSC module, shown in Figure 13, which mates to the Perkin-Elmer Thermal Analyzer 990, has been purchased and set up, but it arrived too late for use this year.

Microradiography. Microradiography was used to statistically determine the average diameter, wall thickness, aspect ratio and wall nonuniformity of a batch of shells. In this procedure, a contact radiograph was made of a set of randomly-selected glass shells, using a modified Flaxitron X-ray chamber operating at 6 KeV for 3 hours. The film used was Kodak 1A high resolution 4 x 5 glass plates. The resulting radiographs of the shells were analyzed with Joyce-Loebel MK-3 densitometer.

Interferometry. Interferometry of shells was used to determine rapidly and statistically the average diameter and wall of a sample of shells. The instrument used is a Zeiss model 46290 interferometer fitted with a Polaroid film back.

Residual Gas Pressure Analysis. As a complement to the analysis of residual gases in shells, the total permanent gas pressure in shells at ambient temperature was determined by the Gas Entrapment in a Viscous Fluid (GEVF) procedure. In this method, shells are glued to a knife-edged fixture and are immersed in glycerin. The internal diameters of the shells are measured by image shearing using a Timbrell Shearicon interfaced with a Reichert Metalograph. The shells are then mechanically broken. The residual gases form bubbles in the glycerin, whose dimensions are determined by image shearing. From the bubble volume/shell volume ratio, the residual pressure is calculated by gas law relationships

4th QUARTER WORK SCHEDULE

	September		October			November			December
	7 14 21		5 12 19		2 9 16 23			6
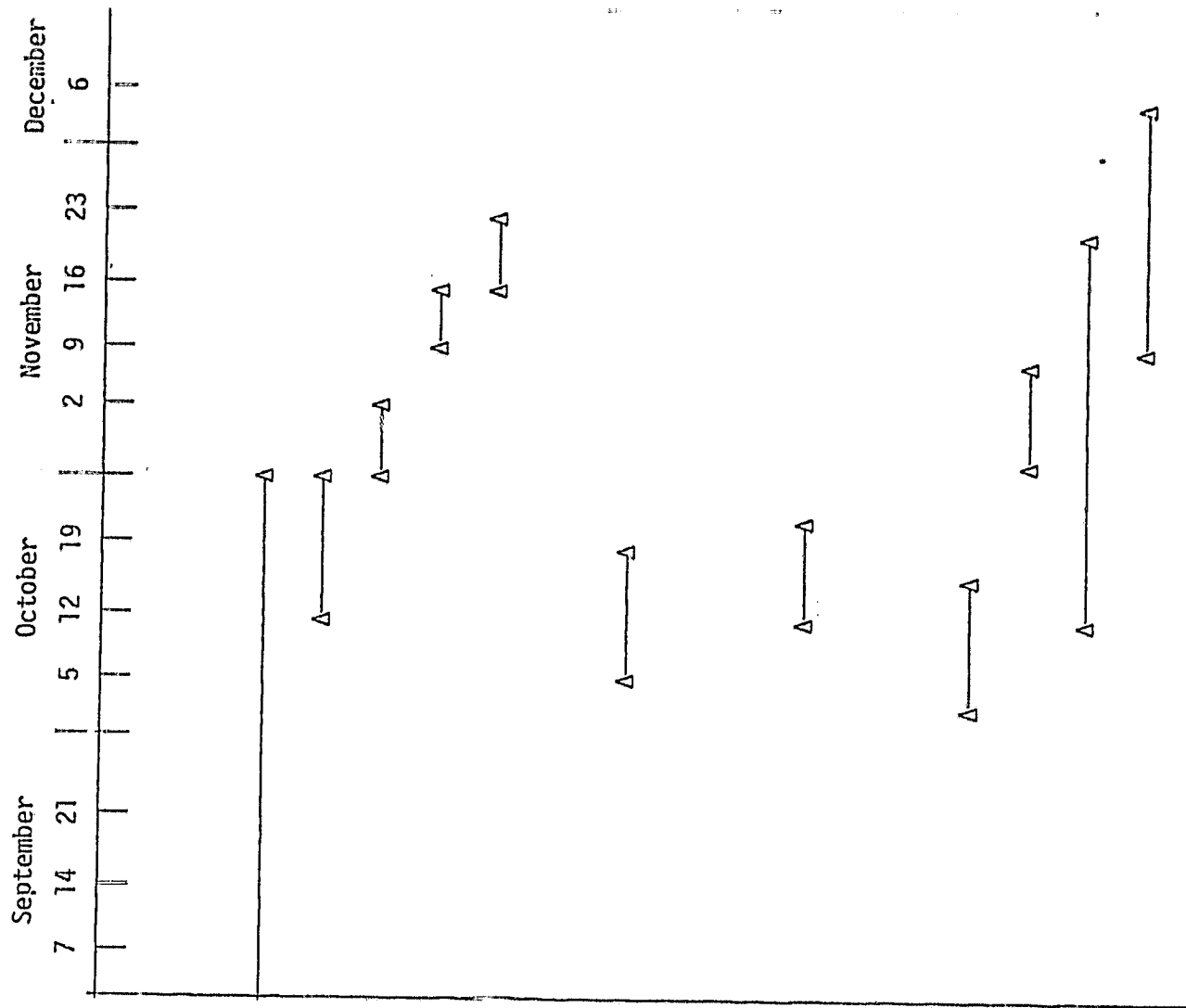
1. Vary H_2O concentration in furnace

   1.1 analyze shells on hand

   1.2 blow shells from metal-organic gel

   1.3 analyze gas in shells

   1.4 blow shells from inorganic gel

   1.5 analyze gas in shells

2. Vary furnace temperature

   2.1 blow shells

   2.2 analyze residual gas - not done, poor yields

3. Surface area analysis of various gels

4. Correlation of physical & chemical events in gel

   4.1 hot stage microscopy of gel

   4.2 staged isothermal PGC

5. Reassessment of accumulted data

6. Quarterly report

TABLE 1

Residual Gases in Shells by Gas Chromatography

Shell Sample	Gel History	Gas In Gel	Gas in Furnace	Relative Concentration, Volume %			
				CO_2	O_2	N_2	H_2O
A	Unhydrolyzed	Argon	Air	68.5	15.2	16.3	N/A[1]
B	Hydrolyzed	Argon	Air	80.5	11.9	7.6	N/A[1]
C	Unhydrolyzed	Air	Air	70.8	18.7	10.5	0
D	Hydrolyzed	Air	Air	79.9	13.3	6.8	0
E	(2)	Air	Air	20.7	25.8	53.4	0

1. Analysis for water not available due to lack of sample.

2. Gel starting material was prepared by evaporation (120^oC) of an aqueous sodium silicate solution in air.

TABLE 2

Pyrolysis Gas Chromatography of Hydrolyzed Gels

Gel Presursor	Gel History	Gas in Gel	Volatiles (by TGA)	Relative Concentration, Volume %								
				CO_2	H_2O	EtOH	CH_3CHO	CO	CH_4	C_2H_4	C_2H_6
C	Unhydrolyzed	Air	17%	4.5	51.4	25.9	6.1	7.3	3.2	1.2	0.3
D	Hydrolyzed	Air	13	9.8	87.9			1.3	1.0		
C'(1)	Unhydrolyzed	Air	20	2.4	45.6	39.6	6.4	2.5	1.7	1.3	0.3
D'(2)	Hydrolyzed	Air	13	8.9	88.6			1.5	1.0		

(1) C' is same as C except analysis made after ∿ 10 months.

(2) D' is a sample of C' which has been hydrolyzed under same conditions as D.

TABLE 3

Comparison of Gels and the Resulting Shells*

Gel, Source and Treatment	Metal-Organic, Unhydrolyzed	Metal-Organic, Hydrolyzed	Inorganic
GEL POWDERS			
Particle Size Distribution	79% 81-102 μm	42% 81-102 μm	15% 64-81 μm
	12% 102-128 μm	56% 102-128 μm	62 81-102 μm
			20% 102-128 μm
GLASS SHELLS			
Yield	12%	35%	46%
Size Distribution	188 ± 60 μm	208 ± 40 μm	148 ± 20 μm
Wall Thickness	3.6 ± 1.4 μm	7.0 ± 4 μm	7.8 ± 1.4 μm
Aspect Ratio (OD/Wall)	62 ± 34	38 ± 17	19 ± 4
Wall Nonuniformity (Average)	15%	16%	50%

*Gels were processed and shells were blown in air.

TABLE 4

Pyrolysis GC of Argon Processed Gels and
Properties of Their Shells

Shell Sample	Gas History	Gas in Gel	% Volatiles (TGA)	Gas Analysis Relative Concentration, Volume %			Yield	Shell Properties		
				CO_2	H_2O	Organics		$\overline{AR}$	$\overline{OD}$ μm	$\overline{W}$ μm
A	Unhydrolyzed	Argon	12.3	1.6	17.8	80.6	7%	48	182	3.8
B	Hydrolyzed	Argon	14.9	1.3	93.9	4.8	21%	64	262	4.1

TABLE 5

Pyrolysis GC of Argon Processed Gels
Exposed to CO_2

Gel Sample	Gel Treatment	% Volatiles (by TGA)	Relative Concentration, Volume %								Comments
			CO_2	H_2O	EtOH	CH_3CHO	CO	CH_4	C_2H_4	C_2H_6	
A	Argon only (dry)	12.3	1.6	17.8	64.0	4.4	6.5	3.3	2.2	0.2	
A'	A exposed to 100% CO_2 (dry)		20.3	42.1	21.2	7.6	7.1	1.7	0.5		
B	Hydrolyzed under Ar	14.9	1.3	93.9	1.5	1.0	1.4	0.9			
B'	B exposed to 100% CO_2	14.4	39.8	39.8	0.4	0.5	+	19.0 →	0.6		Unsieved
B"	B exposed to 100% CO_2		6.1	78.3	0.8	0.9	2.3	10.4	1.2		Sieved
B'"	A exposed to 100% CO_2 and 100% RH simultaneously	19.0	41.6	36.6	0.9	1.2	+	16.7 →	3.0		

TABLE 6

Residual Gases in Shells Exposed to Water Vapor
During Shell Blowing

Shell Sample	Glass System	Shell Blowing Environment	Relative Concentration, Volume %, by GC			
			CO_2	O_2	N_2	H_2O
F	Na, K, B, Ca, Si	Dry air	57.9	18.6	23.5	0
F'	Na, K, B, Ca, Si	$H_2O(g)$ (high concn.) and air	21.3	14.7	30.9	33.1
G	Na, K, B, Si	$H_2O(g)$ (high concn.) and air	88.2	7.5	4.3	0
G'	Repass of G through furnace	H_2O g (high concn.) and air	44.3	17.7	7.2	30.7
H	Na, K, B, Si	H_2O g (high concn.) and air	35.8	17.0	15.7	31.4
H'	Repass of H through furnace	Dry air	54.8	33.7	11.5	0

Proposed Plans for 1980 - 1981

1980 — 1981

	1980				1981		
	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec

HEAT TRANSFER
  Mathematical Model
  Experimental Test of Model

GAS TRANSPORT
  Theoretical Model
  Experimental Test of Model

COMPOSITION EFFECTS
  Three Component Glass
  Four Component Glass

SHELLS FROM LEVITATED GEL (JOINT EXPERIMENTS WITH MSFC)
  Planning
  Levitation Stability
  Heating Rates
  Optimum Residence Time
  Optimum Quench Rate
  Plan KC 135 or SPAR Experiments
  Assess Value of Space Shuttle Experiments

FIGURE 1

DTA-TGA-PMS CORRELATION FOR UNHYDROLYZED GEL
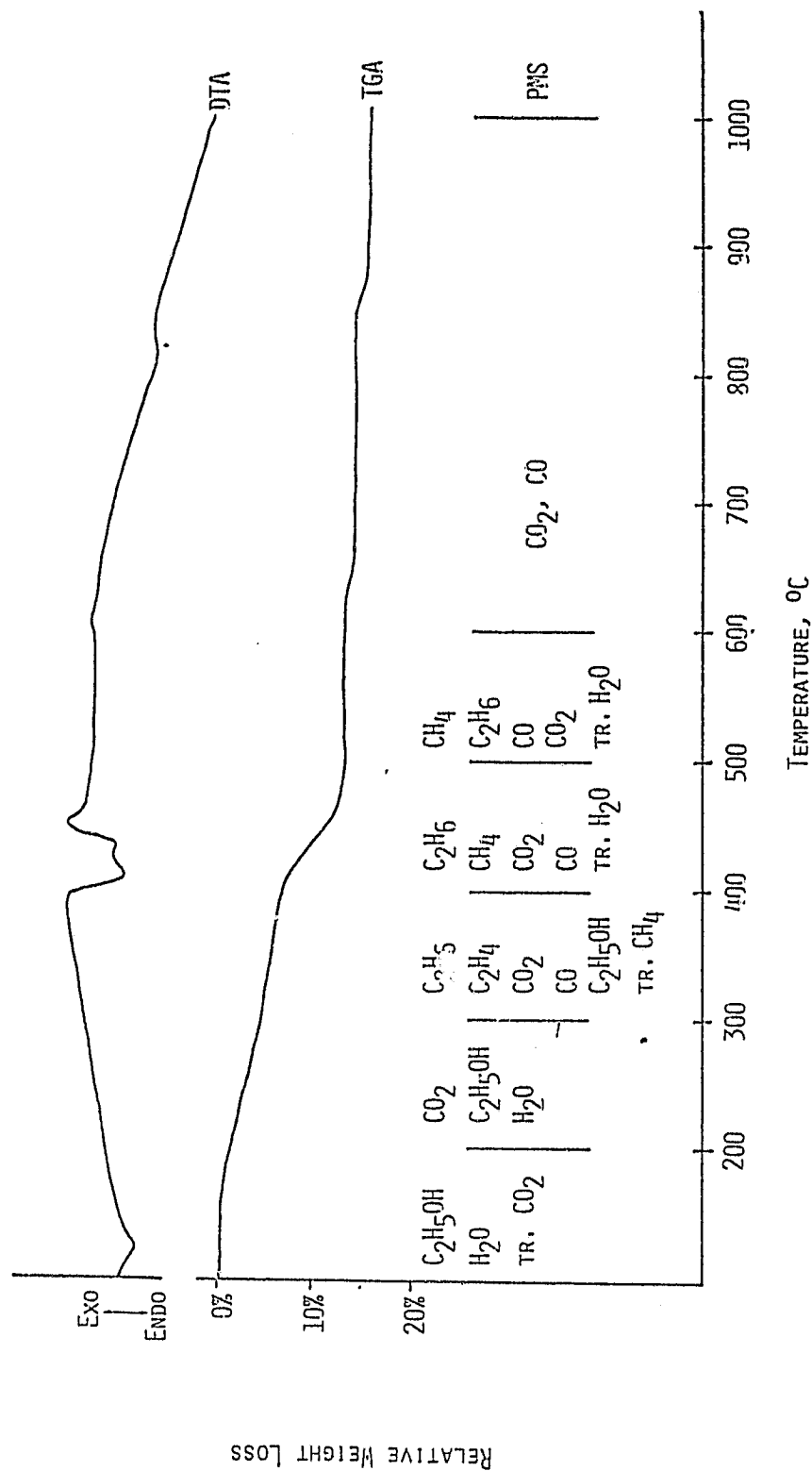
FIGURE 2

DTA-TGA-PMS CORRELATION FOR HYDROLYZED GEL

Exo

Endo

DTA

TGA

0%

10%

20%

RELATIVE WEIGHT LOSS

| | 200 | 300 | 400 | 500 | 600 | 700 | 800 | 900 | 1000 |

TEMPERATURE, °C

H₂O
TR. CO₂
TR. CO

H₂O
CO₂
CO

CO₂
CO
H₂O

CO₂
CO
H₂O
TR. CH₄

CO₂
CO
TR. H₂O
TR. CH₄

CO₂, CO

PMS

FIGURE 3

WATER, % of TOTAL EVOLVED GASES FROM GEL

TEMPERATURE °C

AIR PROCESSED, UNHYDROLYZED

AIR PROCESSED, HYDROLYZED

ARGON PROCESSED, UNHYDROLYZED

ARGON PROCESSED, HYDROLYZED
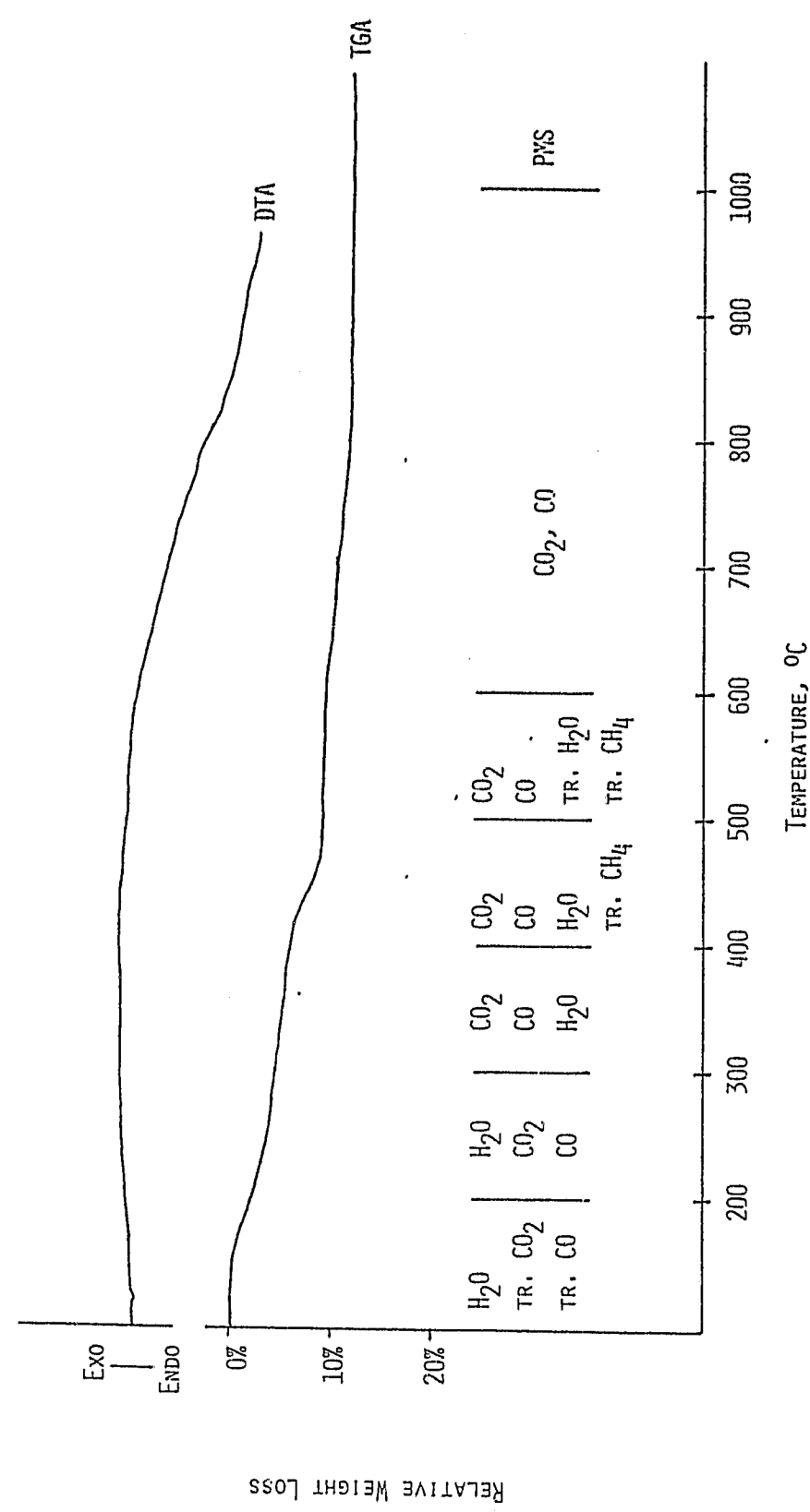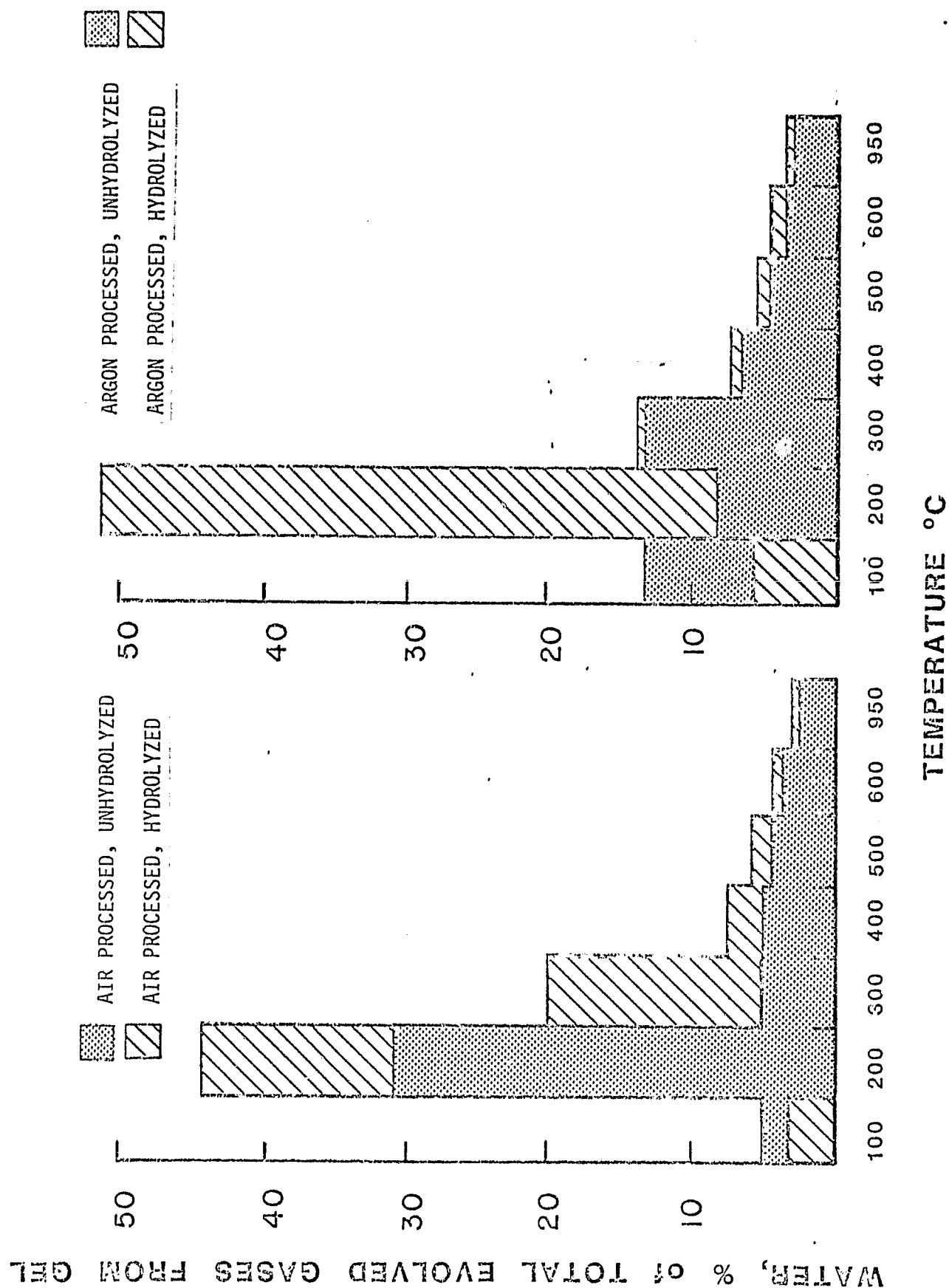
FIGURE 4

Gel Morphology[1]

Gel Sample	Rigid Gel	Sintering	Foaming Expansion	Spheroid	Crude Shell Central Void
E[2]	RT	—	—	150°	300°
B[2]	RT		$150\text{-}200^{\circ}$	$250\text{-}400^{\circ}$	$800\text{-}900^{\circ}$
A	RT	400°	500°	$800\text{-}900^{\circ}$	—

1. Based on observations using hot stage microscopy.
2. Surface area measurements are $\leq 0.1 \ m^2/gm$, close to that for a solid sphere.

Figure 5

POSSIBLE MODEL OF SHELL FORMATION

A
Rigid,
Porous Gel

B
Rigid Gel,
Sintered

C
Foam
Gel

D
Glassy
Spheroid

E
Spheroid,
Central Void

F
Thin-walled
Sphere
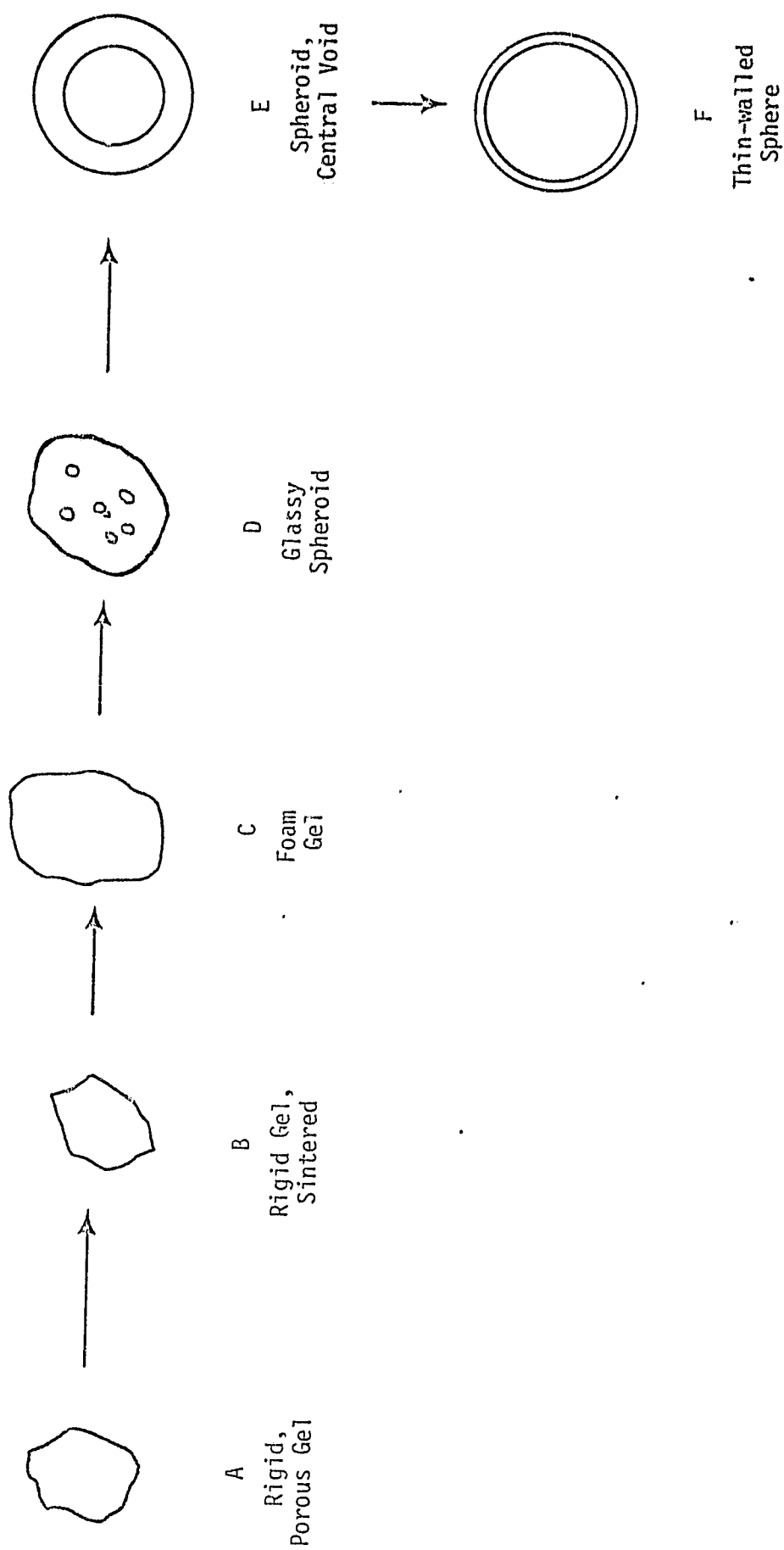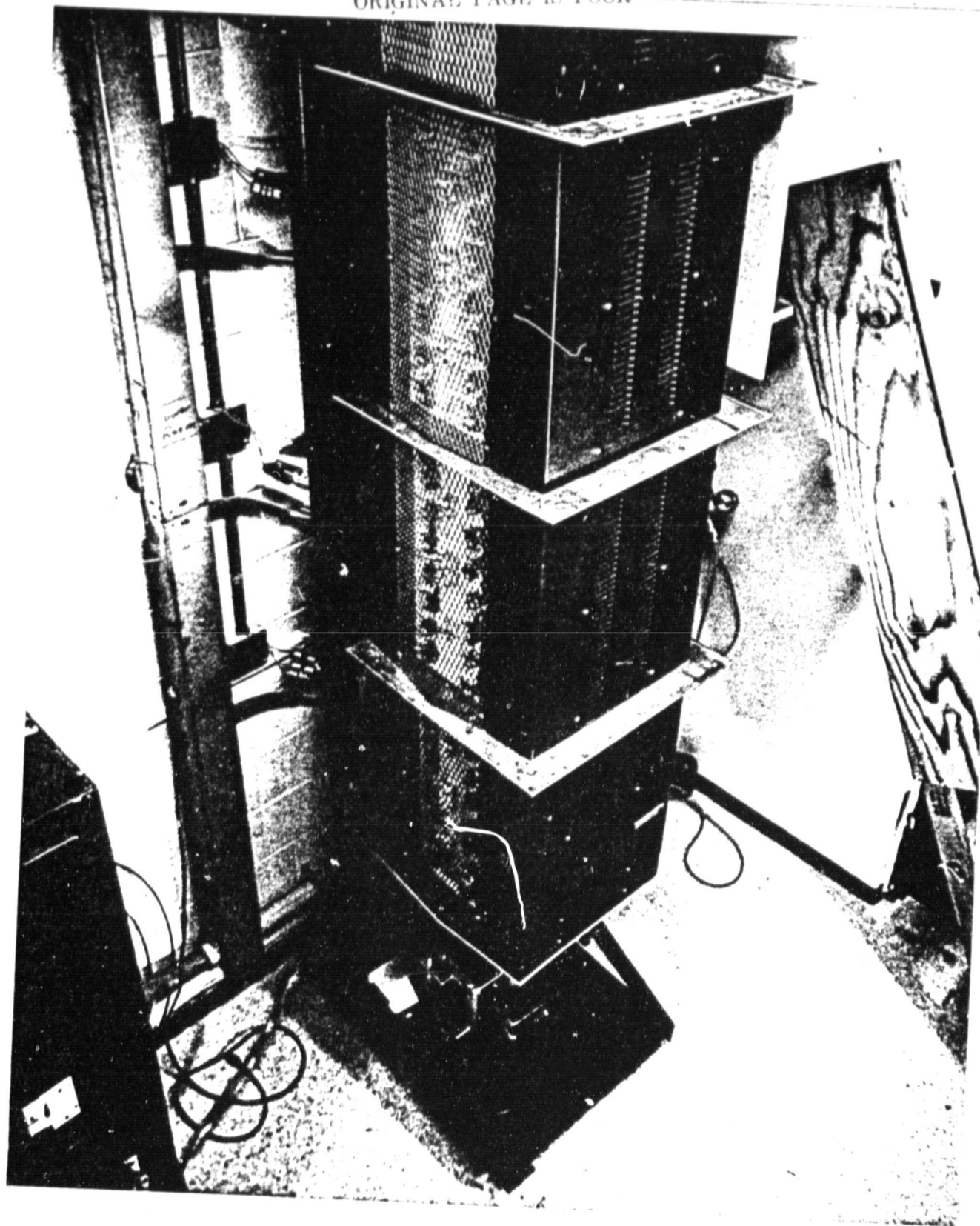
Fig. 6.   Drop Tower Furnace used for manufacturing glass shells.
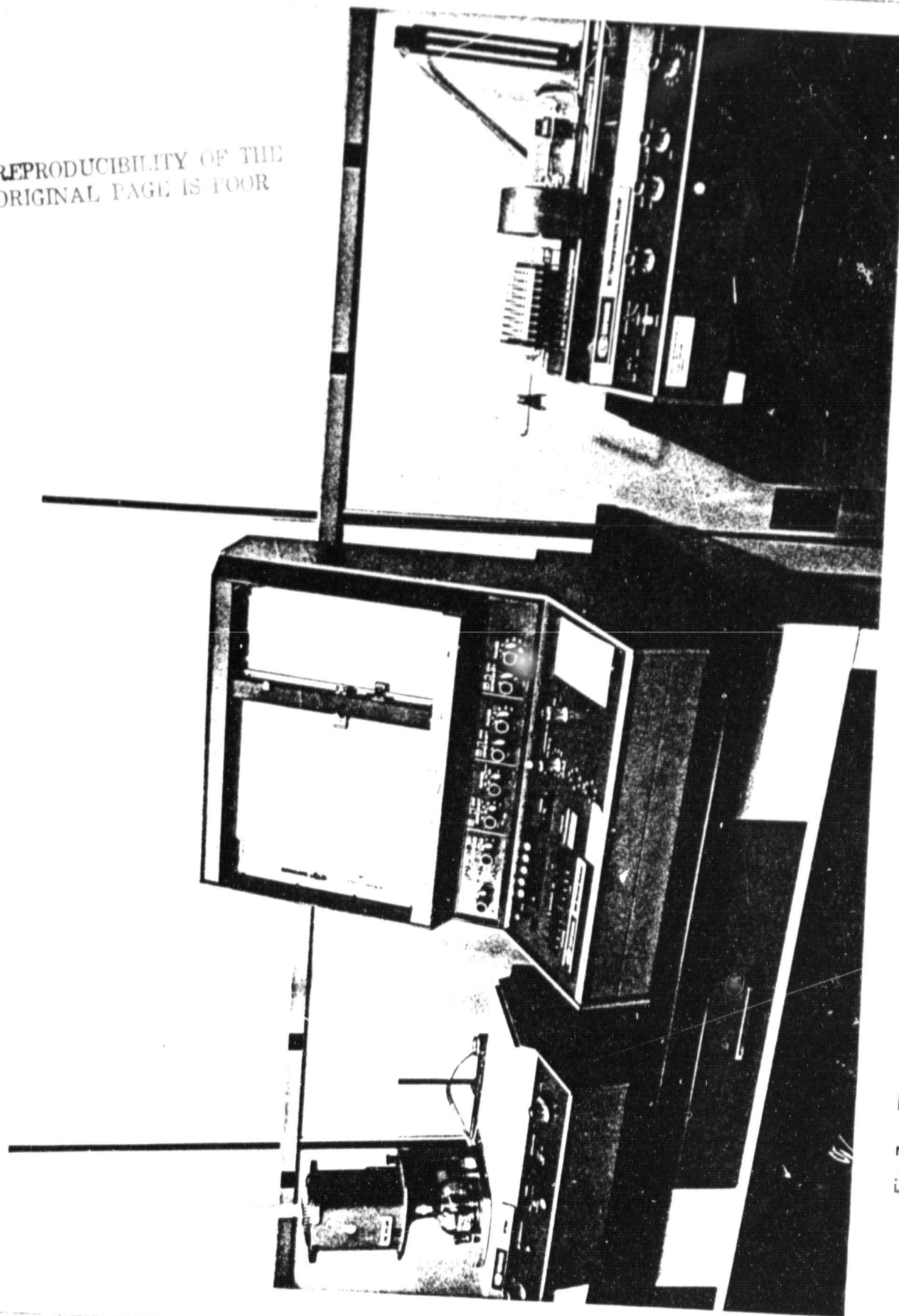
Fig. 7. Thermal Analyzer with thermogravimetric analyzer (TGA) and differential thermal analyzer (DTA) modules.
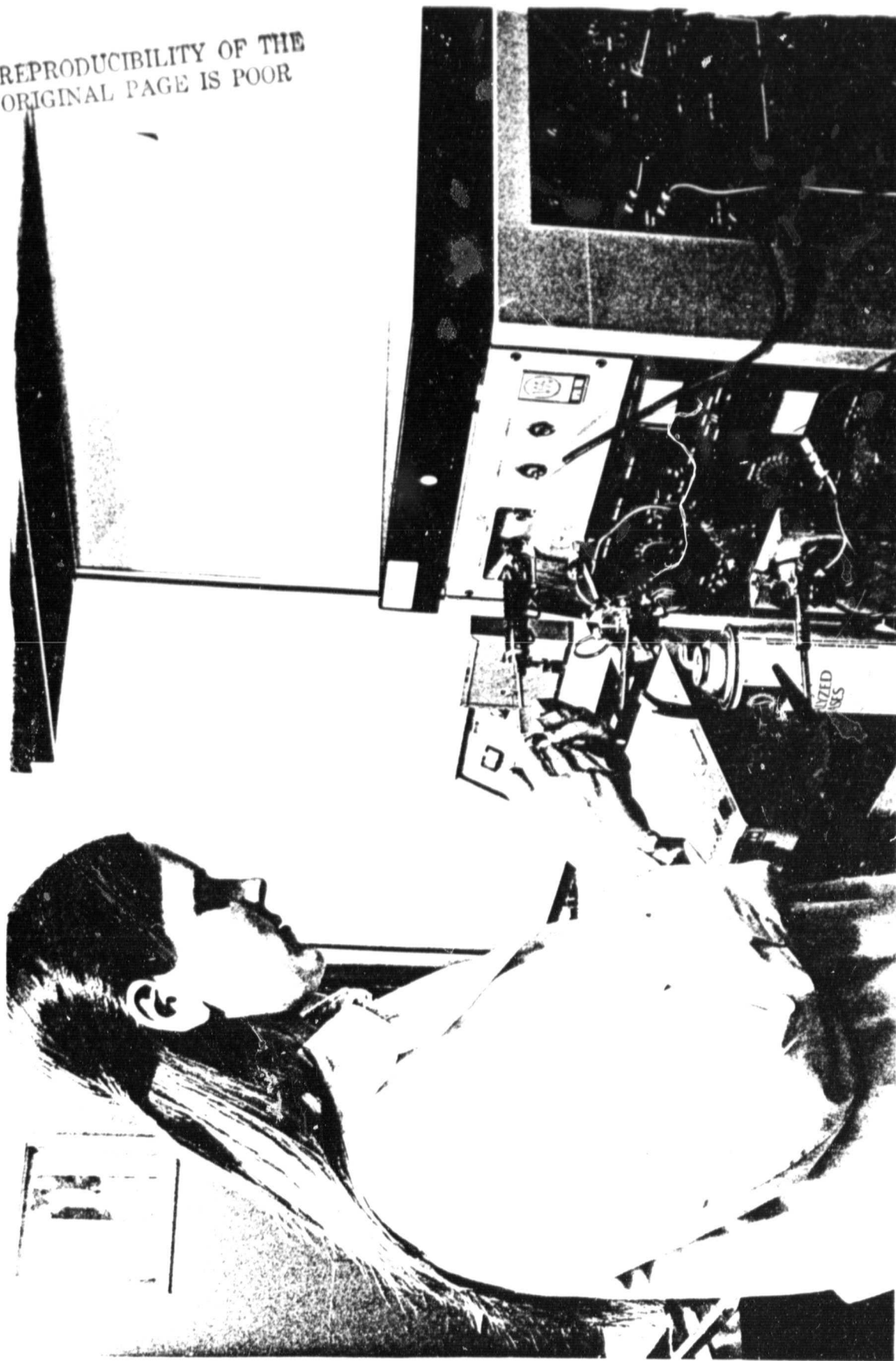
Fig. 8. Pyrolysis gas chromatography for analysis of volatiles from gel pyrolysis.

Fig. 9. Close-up of the gel pyrolyzer.
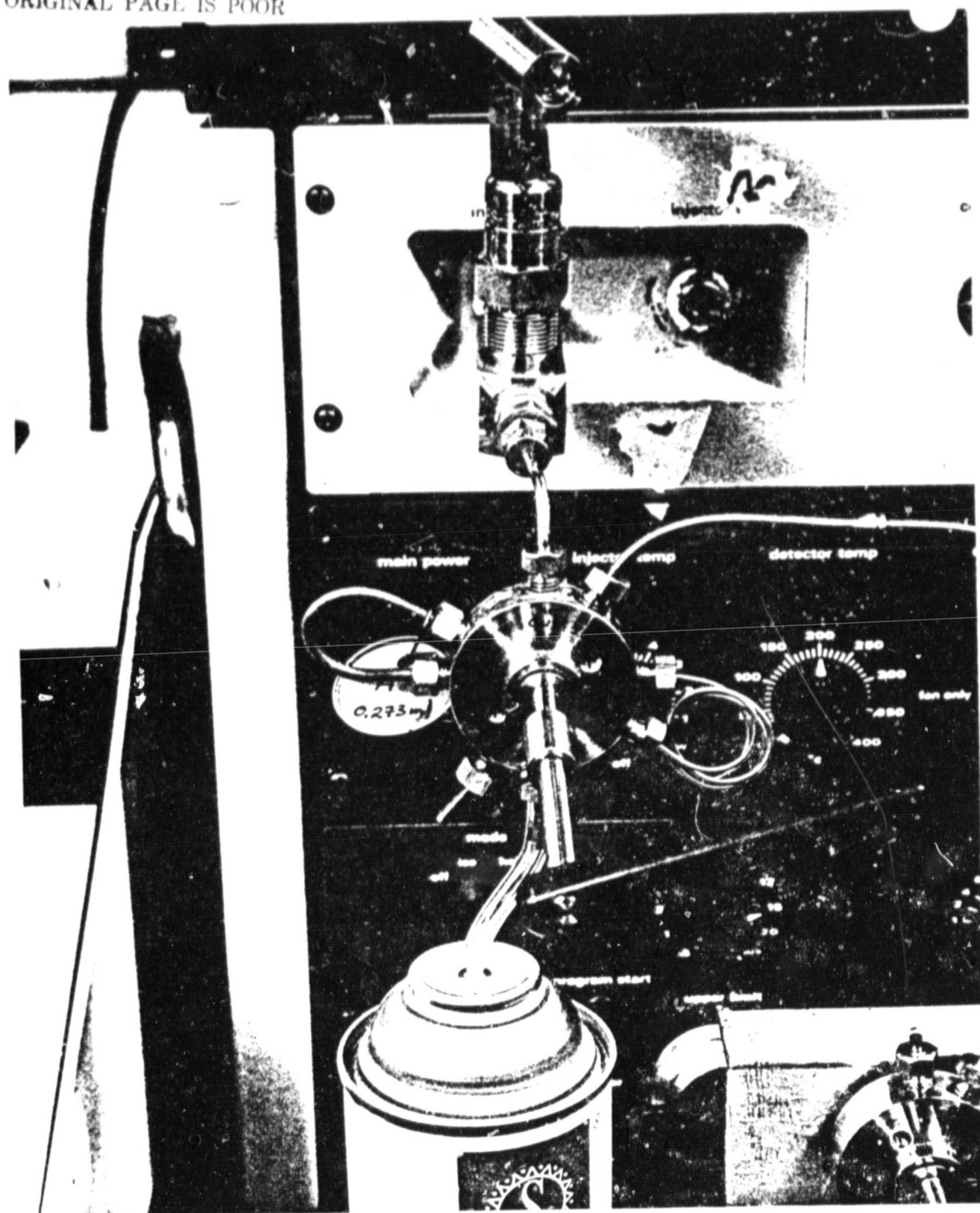
Fig. 10.   Shell crusher assembly and gas chromatograph, for analysis of
residual gases in glass shells
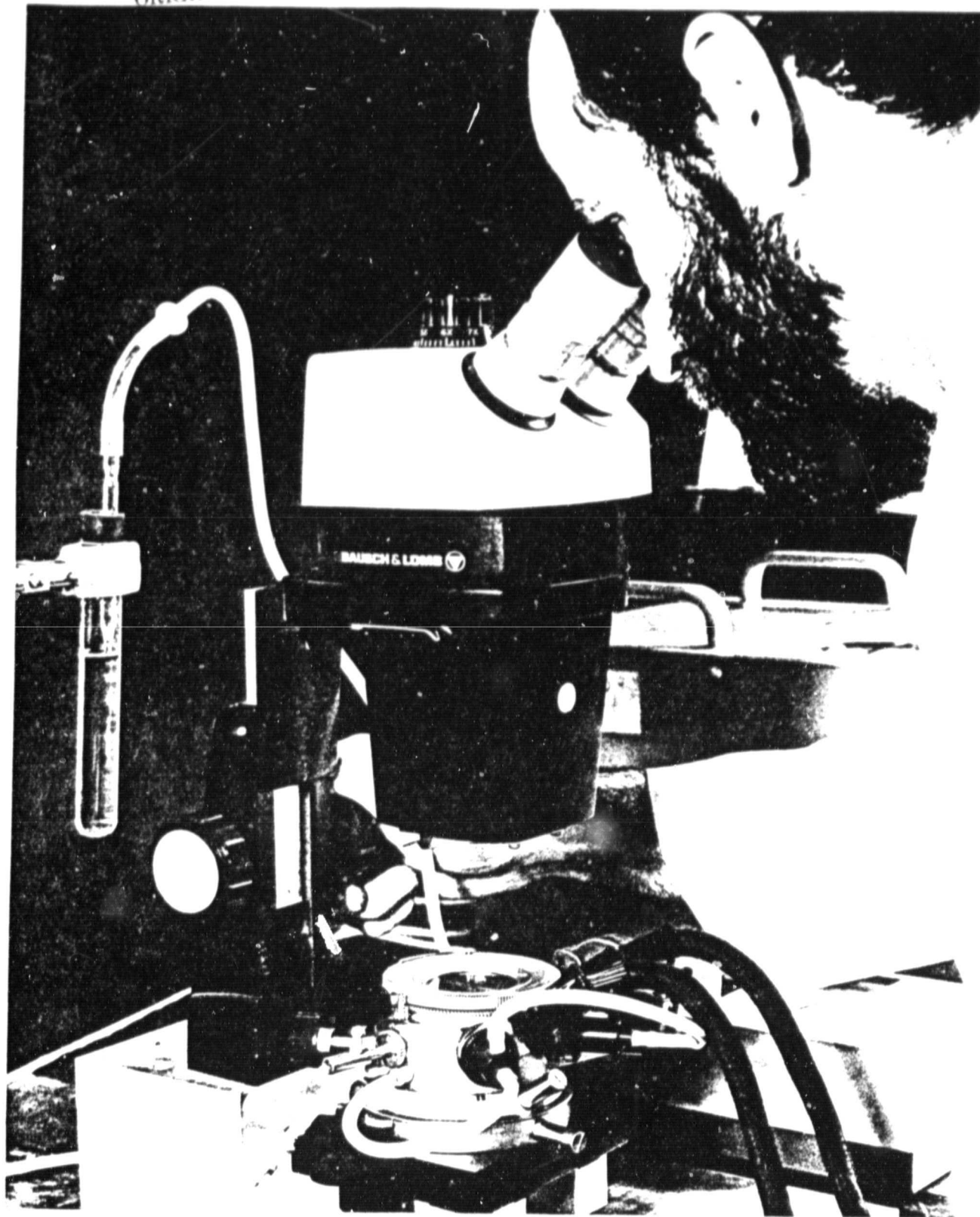
Fig. 11.   Hot Stage Microscope.
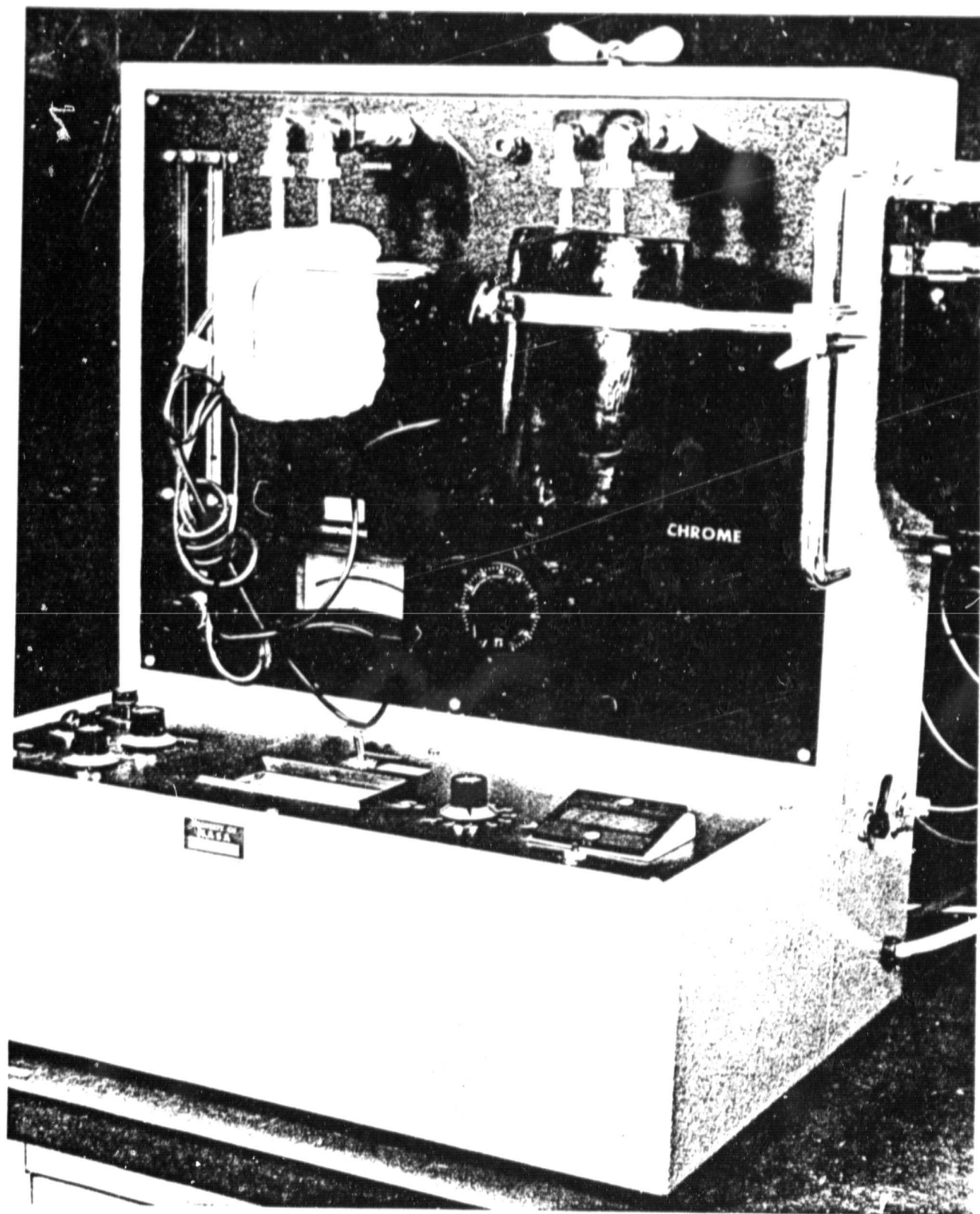
Fig. 12.   Surface Area Analyzer.
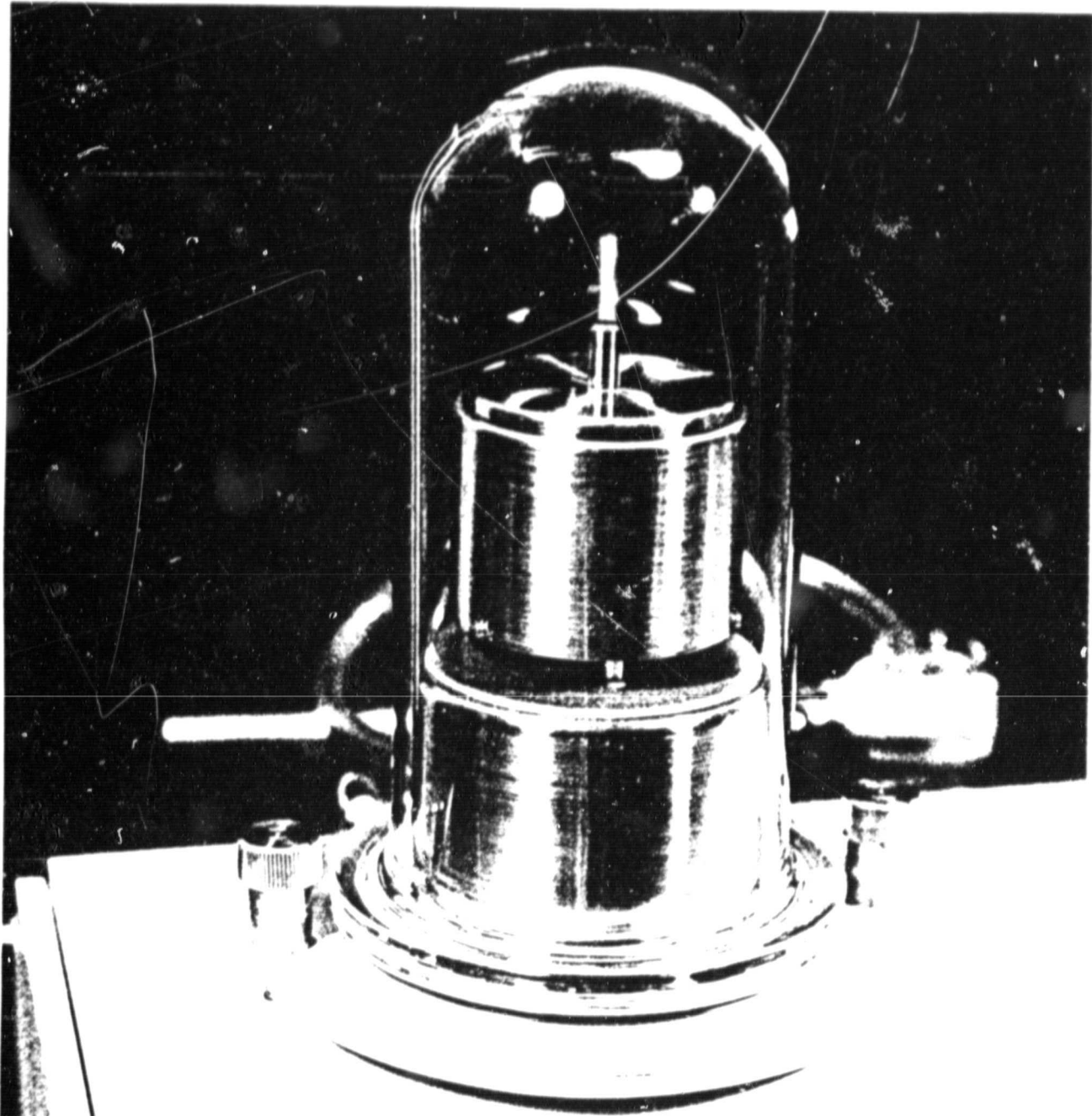
Cell Base

Fig. 13.   Differential Scanning Calorimeter (DSC).