R-56

THERMOGRAVIMETRIC INSTRUMENT

Leo A. Wall and Sidney Straus

ABSTRACT

24997

A thermogravimetric instrument, capable of performing rates of volatilization measurements under both isothermal and non-isothermal conditions, has been constructed and its characteristics studied.

Author

THERMOGRAVIMETRIC INSTRUMENT

INTRODUCTION

Studies on the thermal decomposition of polymers and other materials by the weight-loss methods (thermogravimetry) have accelerated over recent years. The earliest work at this institution utilized a tungsten spring balance[1,2]. Subsequently, a recording balance was also used[3]. However, this balance which had numerous joints was never completely vacuum tight. With both methods, large heavy furnaces were used, and the furnaces were external of the vacuum line in which the polymers were decomposed. With the availability of the recording electrobalance designed to weigh small samples accurately in a vacuum or other known environment, no serious problem in rapid weighing in a vacuum exists. The greatest remaining problem area involves the accuracy, the constancy of the temperature measurements, and the amount of time involved in attaining a precise controlled, and known temperature. Also with the control equipment now possible, there appeared no reason for large furnaces. The apparatus described below appears adequate for relatively rapid and precise non-isothermal (TGA) and isothermal thermogravimetry.

DESCRIPTION OF TGA APPARATUS

The pyrolysis apparatus and equipment are both compact and mobile. All the instruments and glassware are mounted on a 3-ft. square rack that is heavily weighted with a 1/2-in. steel base plate approximately 1 1/2-in. from the floor. The four legs of the rack, one at each corner, are fitted with heavy gauge casters for mobility, however, the entire rack can be firmly stationed by means of four flat 3-in. square discs that can be impinged on the floor and positioned by four individual heavy machine screws. The overall view of the equipment is shown in Fig. 1.

At the top left is the Pirani vacuum gauge (type GP-110) that is bridged to the vacuum system via a gauge tube containing the sensing element. Small internal gas pressures can be measured accurately to a micron or better by measuring the resistance in the system across a wheatstone bridge circuit. The [illegible] electrobalance is situated below the vacuum gauge on the rack. This is the intricate control mechanism which operates and regulates the vacuum balance, encased in a glass chamber, as shown in the upper right in Fig. 1. The electrobalance is based on the null balance principle so that any changes in the sample weight suspended from it, is counterbalanced by electromagnetic force changes via several magnets and a photo tube. Thus the beam remains

in dynamic equilibrium and retains the same position regardless of sample weight loss. In our work, loop A, the most sensitive weighing point on the beam, was used to determine polymer weight losses during pyrolysis of about 1-20 mg. About 250 mg weight of wire and crucible, in addition to the sample weight, is suspended from loop A. The precision on this loop is rated as a tenth of a micron or better.

The Cahn controller is wired to the Brown electronic recorder, shown below it in Fig. 1. The recorder operates automatically with two pens; a red one of 10 mv sensitivity plots the sample weight loss and a purple one of 50 mv that charts changes in the pyrolysis temperature within the furnace. Both slopes can be read directly on the chart paper in mg and mv respectively.

The Gardsman Pyrometric Controller (Model JGP) is situated on the left, in Fig. 1, below the recorder. It consists of an upper portion, the temperature indicator scale and the lower program controller including a pre-set cam. The cam shown in Fig. 1 controls a TGA heating operation of the furnace for 5 hr; 2 hr at 200 °C, 3 3/4 hr to regulate uniform temperature rise from 200 to 600°C and 15 min to return to the 200°C start. The switch is in the "on" position for this automatic temperature regulation. For isothermal analysis at a specific temperature, the switch

is in the "off" position, and the approximate desired temperature is set with the red pointer on the temperature scale. The temperature of the furnace is regulated between the two, 5 amp variacs shown to the right of the pyrometric controller on the panel. The voltage settings on the upper and lower variacs depend on maintaining an equilibrium between the green indicating pointer and the preset red pointer on the temperature chart. A relay switch designates the higher or lower voltage to be used and the corresponding current is recorded on the a-c ammeter set between the two variacs. Generally the higher voltage variac is about double the lower voltage variac and the maximum current needed is about 2.6 amp.

Beneath the panel on the left, not shown in Fig. 1, sets a 1/3 hp Welch fore pump on the 1/2-in. steel plate. The pump, in turn, is attached to a large glass contained oil diffusion pump capable of maintaining a vacuum of 4×10^{-7} mm of Hg. The top portion of the oil diffusion pump is shown in the background immediately to the right of the lower and middle panel. Coolant may be added to the glass well shown. The variac at the lower right is set at 108 v and maintains the heating rate of the oil pump at a current of 1.9 amp as can be observed in the small ammeter to the left of the variac in Fig. 1. A small commercial blower, set behind the panel, directs a stream of cold air at the upper oil stream in the oil pump to hasten condensation and increase the efficiency of the pump.

A compact arrangement of glass apparatus, including the housing for the internal furnace, a cold trap and several outlets to collect volatile polymer fragments is shown on the right beneath the Cahn balance assembly in its cradle. Both gas and liquid volatiles can be collected at these outlets, in suitable containers, for mass spectrometer, infrared or gas chromatography analysis.

CONSTRUCTION OF FURNACE

The key to the pyrolysis potential of the apparatus is lodged in the furnace which was designed and built at the National Bureau of Standards. It operates in a vacuum and has the capability of attaining the desired pyrolysis temperature within 3-5 min after starting from room temperature. With the Gardsman controlling, the temperature can be maintained constant to within 1°C. The furnace, encased in a glass housing, can be seen in Fig. 1 at the middle right.

It consists of two concentric slotted 1/16-in. stainless steel plates, the outer one, 1 1/2-in. in diameter and the inner one, 1 1/4-in. in diameter and both 8-in. long. Two 1/2-in. steatite discs (Pyrophylite), 1 7/8-in. in diameter, position the plates at top and bottom. An overall and top view of the heater can be seen in Figs. 2 and 3.

The narrow grooves in the plates measure 3/32-in. every 1/2-in. of stainless steel. They are staggered between the inner and outer plate so that the heating wires are not

visible from the side. This permits efficient heating and also effectively allows any volatiles to diffuse rapidly from the hot zone to the glass cylinder which could be encircled with liquid nitrogen. There are three 1/4-in. cutout grooves at the outer rim of both steatite discs to secure the thermocouple wires encased in flexible glass spaghetti. The thermocouples protrude from an alundum tube centrally positioned in the furnace by a 9/32-in. steatite plug inserted into the bottom steatite disc. The thermocouples consist of a No. 28 gauge Iron-Constantan thermocouple joined to and controlling the proportionating controller and a No. 28 gauge Chromel-Constantan thermocouple connected to both the Brown recorder and a Leeds and Northrup potentiometer.

The heating wires, No. 20 Nichrome, are wound tightly between the two discs. There are sixteen 1/32-in. openings equispaced about the inner part of the discs through which the wires are secured. Individual wires can be tightened at the top by means of set screws. A cross section of the inner portion of the furnace is shown in Fig. 4 and the set screw arrangement can be seen in Fig. 3. The overall heater is fitted with six 1/16-in. Inconel springs; three equispaced just below the top disc and secured in it, and similarly, three above the bottom disc to expand and contract with respective heating and cooling of the furnace. The springs are particularly important to the successful operation

of this heater in a vacuum since they neutralize the expansion and contraction of the Nichrome heating wires and prevent shorts. Four of these springs can be seen in Fig. 2.

The furnace is suspended in the pyrex glass apparatus by means of two 3/32-in. copper wires that enter the glass as tungsten electrodes and are connected to the top of the heater at opposite posts. One post secures the stainless steel outer plate and the other, the inner plate. The polymer sample is loaded into a small 190 mg Vycor crucible which is suspended from the A-loop of the beam by means of 2-3 mil Nichrome wires and a small intermediary glass wire. The crucible swings freely in the internal center of the vertical furnace shown in Fig. 2. The pre-set thermocouples, mentioned previously, are positioned immediately beneath the Vycor cup, approximately 1-2 mm away.

Temperature Characteristics of Furnace

The operating characteristics of the furnace with the pyrolytic controller were studied. A fixed voltage was set on the higher reading variac linked to the controller, and the rise in temperature of the furnace from room temperature was read on the Leeds and Northrup potentiometer. Temperature readings were made at 30 to 70 volts with 10-volt intervals. Fig. 5 indicates the results of these findings and the points show the time interval of the readings. At 30 volts, the rise in temperature leveled off at about 340°C after about 40 min. The most rapid rise in temperature was obtained at

70 volts, 2.6 amp. The furnace temperature attained 300°C in less than 2 min, 400°C in 3 min, 500°C in less than 5 min, and 600°C in about 12 min.

At the 60-volt setting, two different determinations were made. In one case, the outside of the furnace in the vacuum system was at room temperature, as in all the other cases, and another where a liquid nitrogen container encircled the heater. Fig. 5 indicates that the temperature rise between the two up to 450°C was similar whereas at the higher temperatures, the difference was less than 10°C. Temperature differences outside the vacuum system have very little effect, if any, on the efficiency of the furnace.

In most previous pyrolysis studies, the temperature and weight of the sample under thermal decomposition has been the critique among various investigators. Sample size and composition of the polymer under study presents numerous problems in determining temperature changes on heating, and the embedding of a thermocouple in the sample becomes most impractical and inconvenient on a day-to-day experimentation. Our previous pyrolysis experience has indicated that a fixed thermocouple directly beneath the bucket containing the sample is most feasible and adaptable. Moreover, a sample size of 10 mg or less eliminates spattering and violent eruptions of chunks of sample on thermal volatilization.

In the current research problem, additional studies were made to pinpoint and calibrate any fixed thermocouple we intended to employ. A temporary calibrating thermocouple, No. 28 gauge Chromel-Constantan, was thrust into individual 10 mg samples of polyethylene and polytetrafluoroethylene. The fixed thermocouple, of the same gauge and composition, was positioned underneath the crucible containing the sample, about 1 to 2 mm away. TGA pyrolyses studies were made on the samples from 200 to 600°C with a rise in temperature of 1.78°C per minute. The fixed and calibrating thermocouples were attached to two different Leeds and Northrup potentiometers and read at similar heating intervals. In the case of both polymers, the difference between the two sets of thermocouples varied between 2.5°C and 3.5°C, with an average of 3.0°C, during the entire temperature rise and decomposition of the sample. When the fixed thermocouple was centrally located, just below the center of the crucible, most consistent temperature readings were obtained. Moreover, it was determined that similar temperature differences were had if the sample bucket was raised centrally in the heater to almost 2 cm above the fixed thermocouple. A temperature gradient did not exist, on pyrolysis, between the sample and the fixed thermocouple until they were almost an inch apart.

The calibrating thermocouple in the sample read higher in all cases and a correction of +3 °C is to be made to any temperature reading on the fixed thermocouple positioned 1-2 mm below the bucket.

Adjustment of the Weighing Mechanism.

The Cahn balance required several preliminary adjustments and settings in order to operate for both the TGA and isothermal studies. It was necessary to counterbalance all the weight suspended from the A-loop on the weighing arm, the crucible and wires, with a similar weight on the C-loop. A zero reading on the Brown recorder chart could thus be obtained. This weight was 244 mg in this particular case. The Mass Dial Range on the Cahn controller was set at 20 on the A dial and a Mass of .500. When a 10 mg weight is placed in the crucible, the weight loss can be read directly on the chart in milligrams from 10 to 0, on positioning the Recorder Range at 1. For a 20 mg weight, the Recorder Range is positioned at 2 in order to make best use of the recorder chart.

REFERENCES

1. S.L. Madorsky, J. Polymer Sci. 9, 133 (1952).
2. S.L. Madorsky, Vacuum Microbalance Techniques (Plenum Press Inc., New York, 1962), Vol 2.
3. S.L. Madorsky, J. Research NBS 62, 219 (1959).

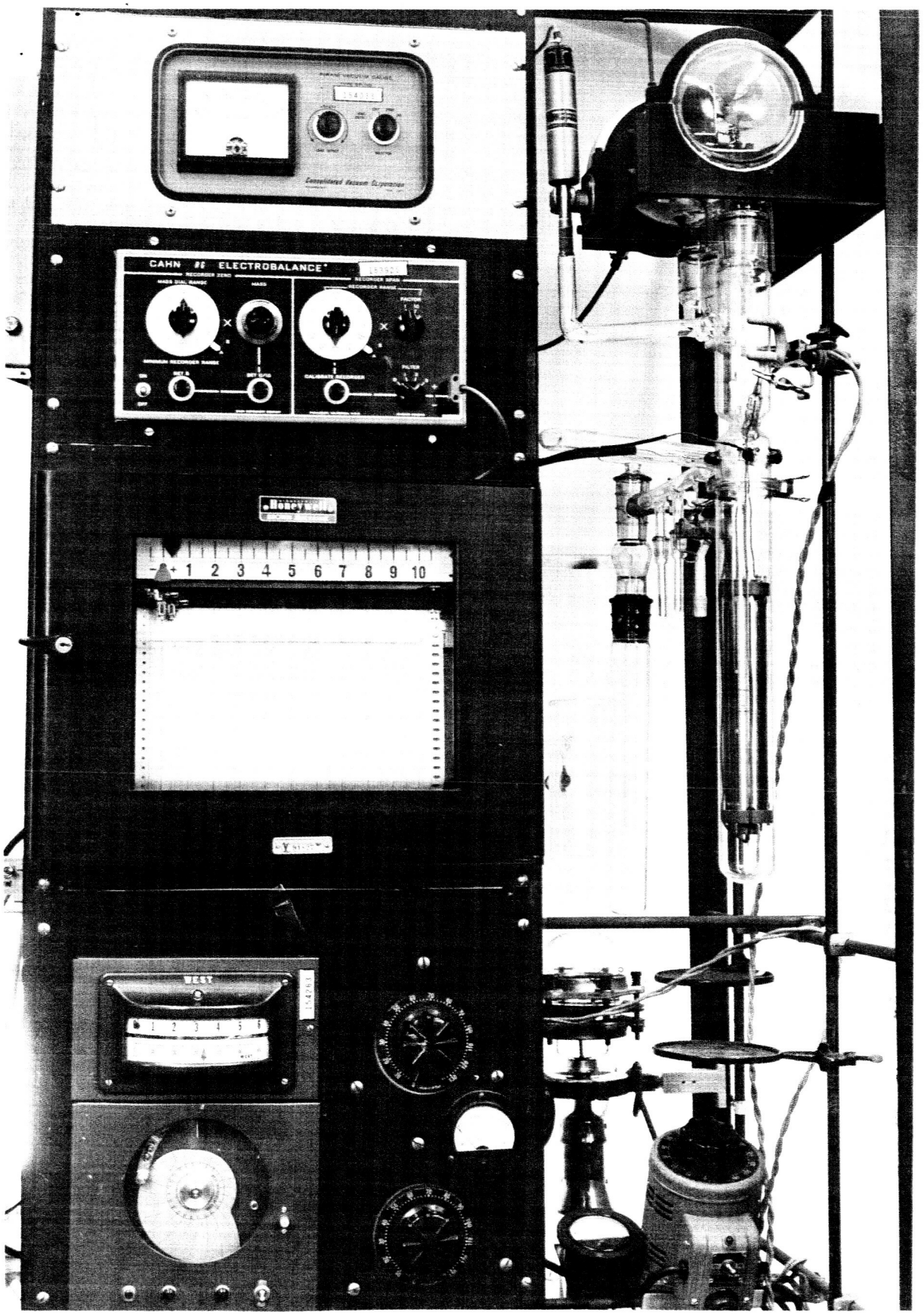


Figure 1. Thermogravimetric Instrument.

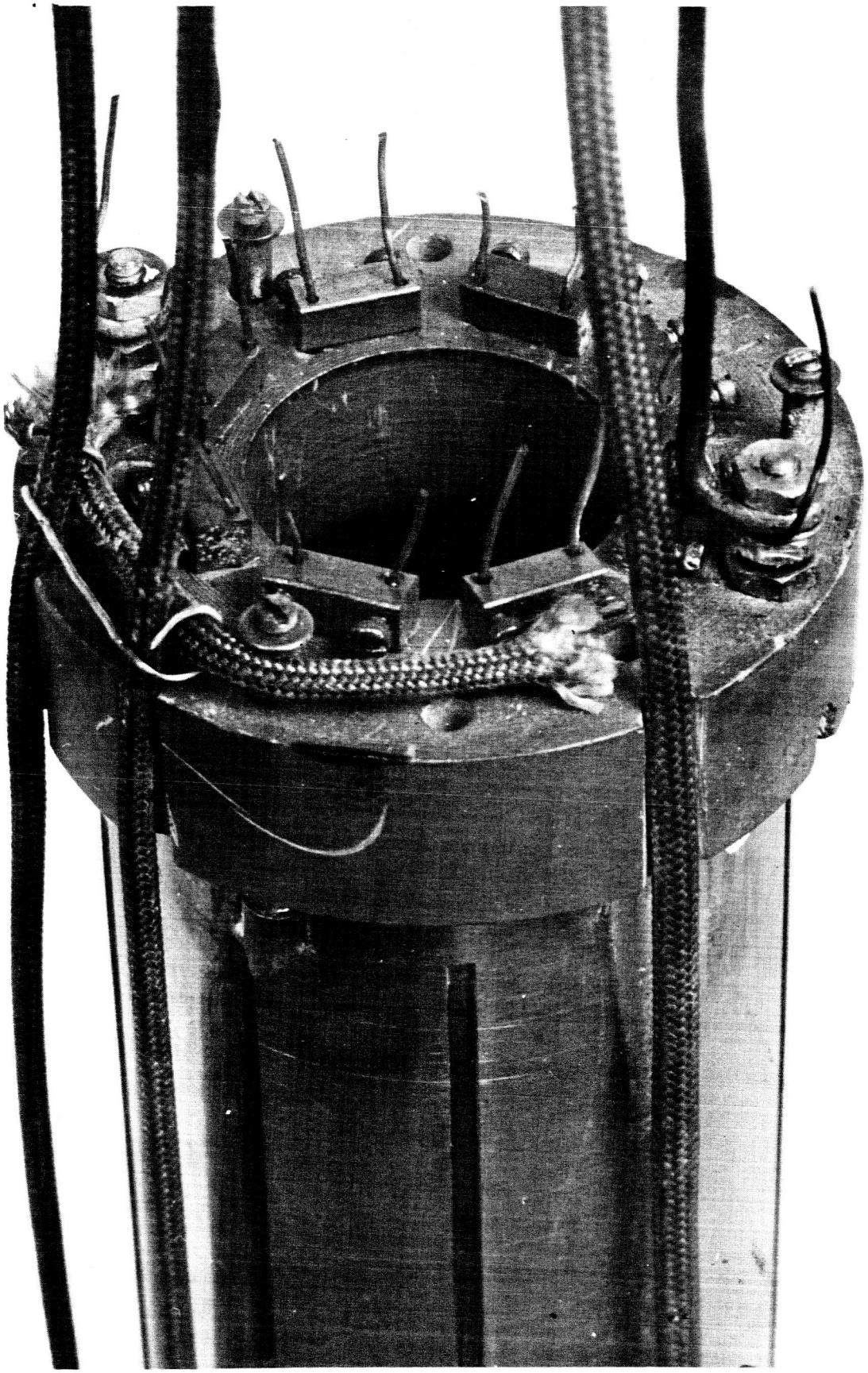


Figure 3. Detail View of Upper End of Furnace

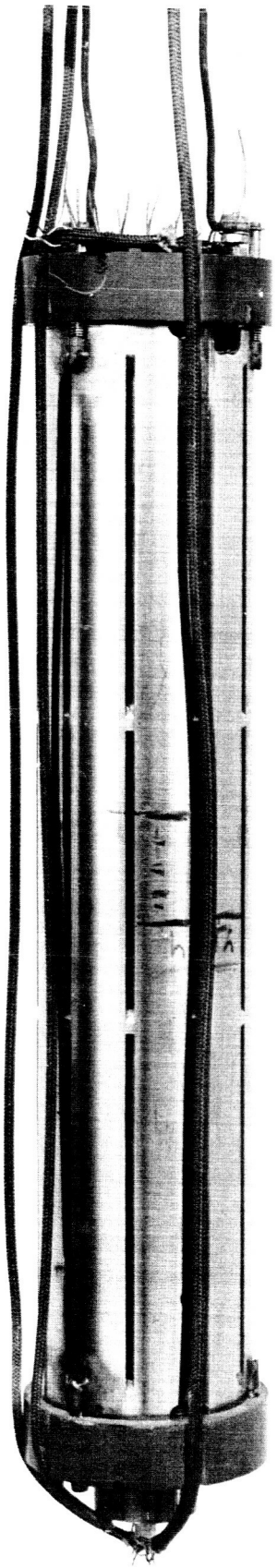
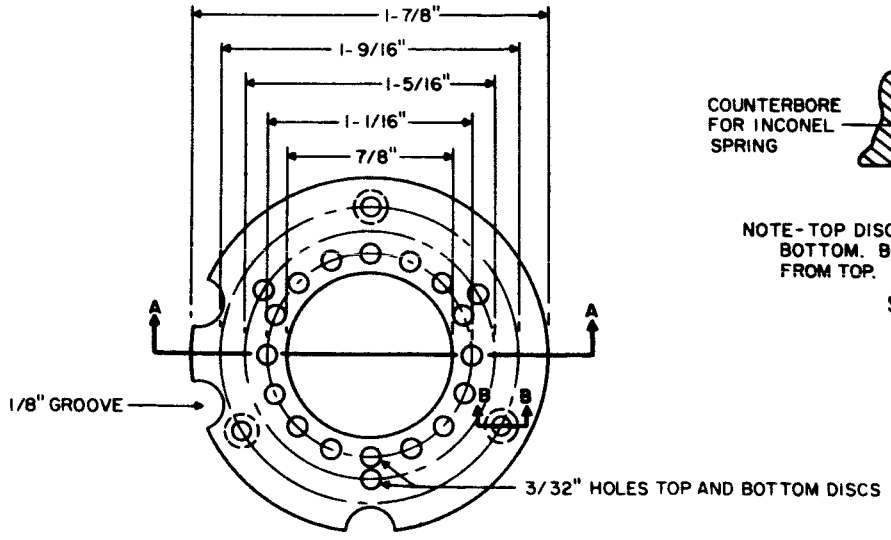
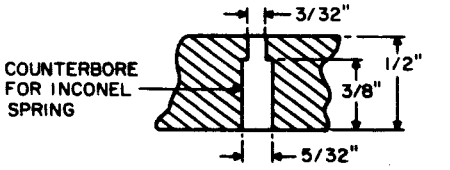


Figure 2. Detail View of Furnace

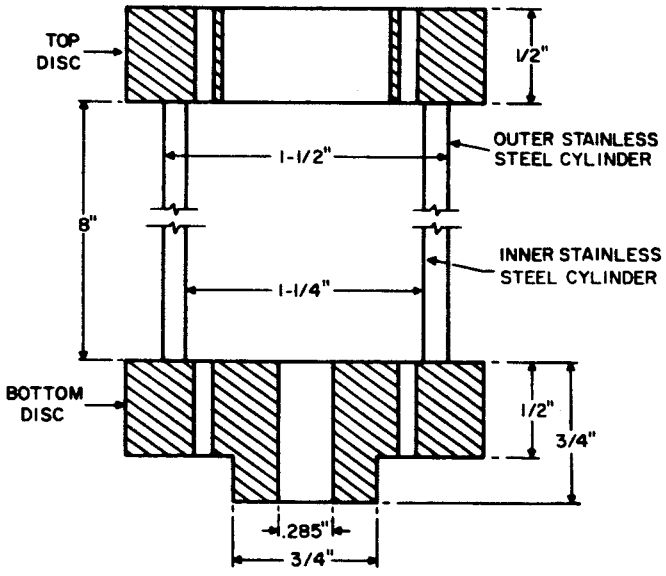


TOP VIEW

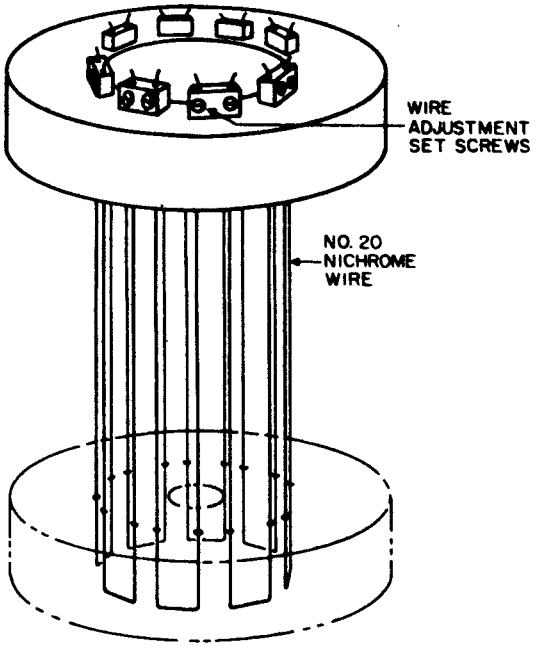


NOTE - TOP DISC, COUNTERBORE FROM BOTTOM. BOTTOM DISC, COUNTERBORE FROM TOP.

SECTION B-B



SECTION A-A



HEATER WIRE INSTALLATION

Figure 4. Furnace Construction

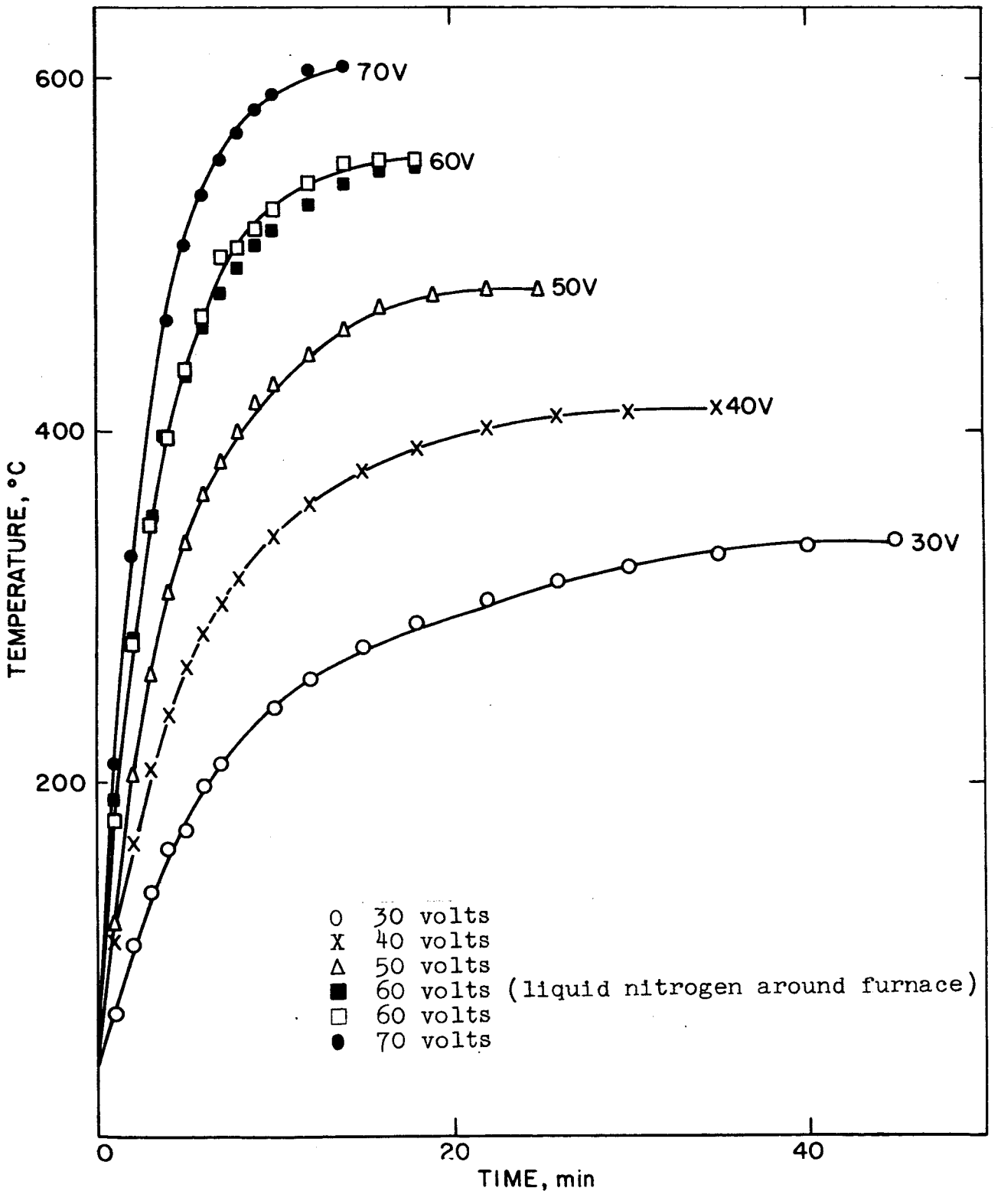


Figure 5. Temperature Rise in Furnace of Various Voltages