3) CAHN Balance Pneumatics and Operation

To evaluate the rate at which a catalyst sample will absorb a particular gas or vapor the following procedure can be employed. A 40 milligram sample of catalyst is placed on the left-hand balance pan. A sample pan enclosure is placed over the sample. The activation oven is then placed over the sample enclosure. The operator then runs program ONE.EXE. This causes operational state 1 to be energized which opens the sorbate release solenoid valve shown in Figure 46. It also opens the rough down pump solenoid valve. In this state a path is opened from the current to torque transducer section to the pneumatic section of the Cahn balance system and from the pneumatic section to the mechanical vacuum pump utilized to evacuate the system. Within 10 minutes the system pressure is reduced below 100 microns. The program TWO.EXE is then run which evokes operational state 2. In this state the system continues to be evacuated by the rough down mechanical vacuum pump and the temperature program for the activation oven started. Once the sample reaches 300 C about 1 hour, it has released the majority of gas held in its internal pore structure. At this time program THREE.EXE is run and operational state 3 is in effect. In this state the sorbate release solenoid valve is closed, the rough down pump applied to the pneumatic section, the diffusion pump applied to the current to torque

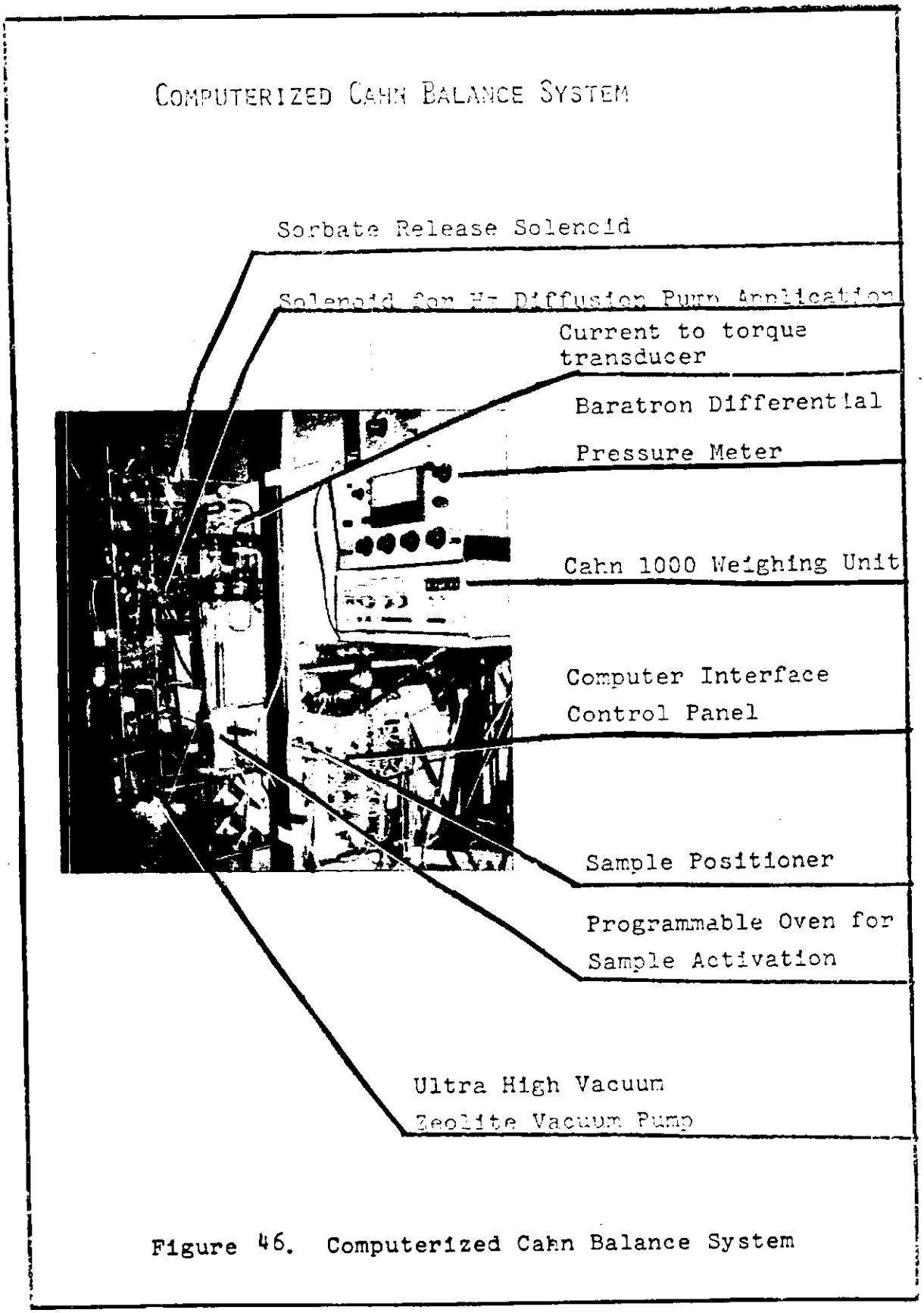

Figure 46. Computerized Cahn Balance System

transducer section, and the temperature program continued. This enables the sample to be held at minimal pressure during the final stages of its activation and makes the rough down pump responsible for holding the pneumatic section at a reasonable vacuum. Thus, frequent small leaks occurring in the pneumatic section because of the multitude of valves contained in this section does not effect the pressure over the sorbant during the final stages of activation. Once the sample is completely activated program FOUR.EXE is run invoking state 4. In this state the rough down pump is removed from the system through the closure of the rough down pump valve. The diffusion pump connected to the pneumatic section to reduce the pressure in this section to below 10 microns and the sample oven is shut off. Once the programmable oven cools to the temperature at which the sorbtion rate curve is desired, program FIVE.EXE is executed. In this state the entire system continues to be evacuated by the diffusion pump and the sample pan is lowered to come into physical contact with the base of the sorbant chamber. Because the sample is held in vacuum it cannot cool by convection or conduction. The rate of cooling by radiation varies with the 4th power of the temperature difference. As it approaches the temperature of the sample enclosure, therefore, its rate of cooling would continue to decrease. For this reason the sample positioner was added such that the sample pan could be placed in conductive contact with the metallic base of the sample enclosure. This not only

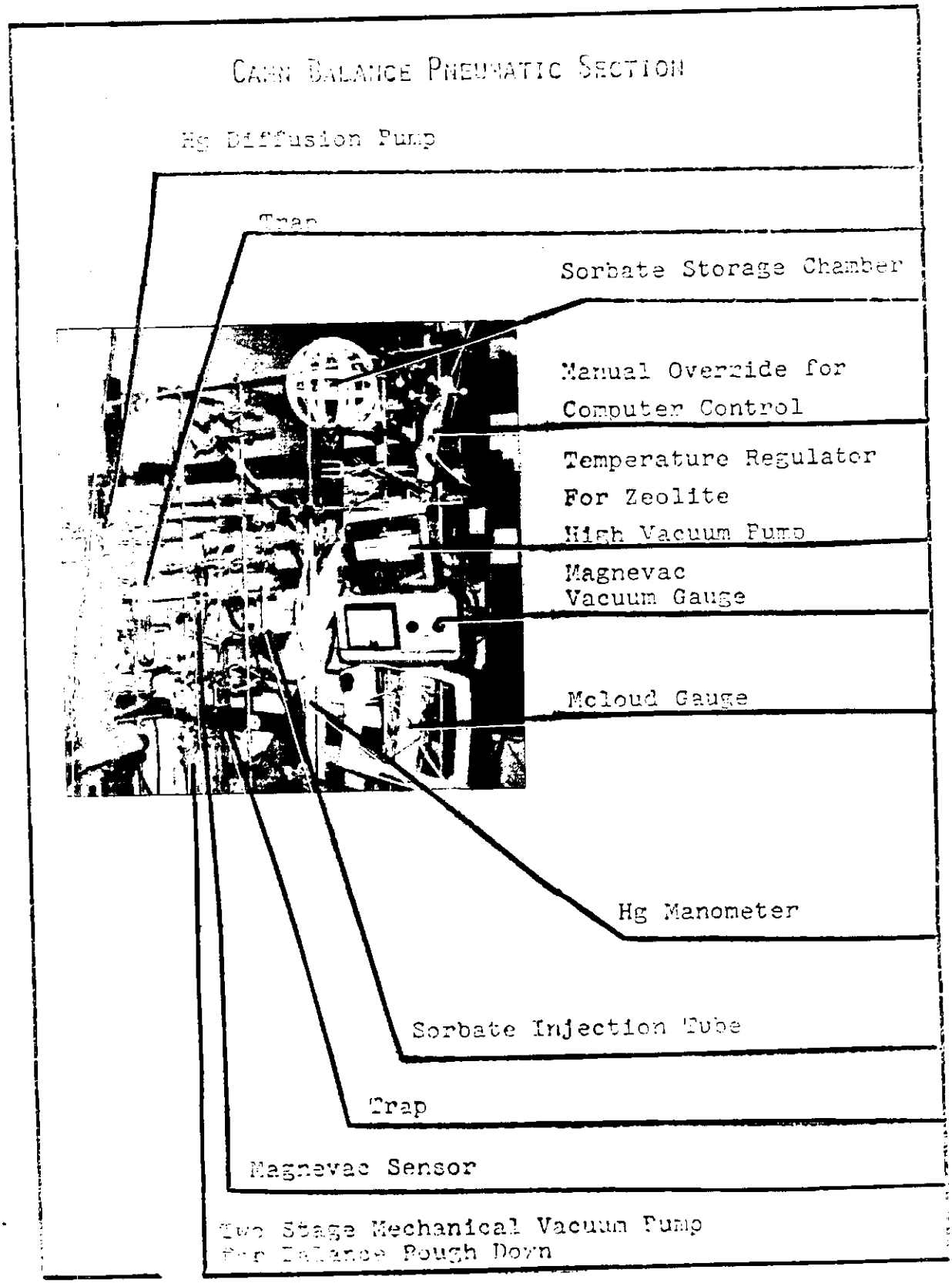

Figure 47 . Cahn Balance Pneumatic Section

provided more rapid cooling of the catalyst sample but also a more accurate knowledge of the temperature of the sample.

Finally, program SIX.EXE is executed which raises the sample pan, closes the sorbate release valve, thereby separating the pneumatic section from the current to torque transducer section. In operational state 6 the diffusion pump continues to evacuate the current to torque transducer section leaving the pneumatic section ready to be filled manually with the desired pressure of the desired sorbate. Once this is accomplished, program CAHN40.EXE is executed. This program sets up the clock and A to D converter to collect data on an interrupt basis. 50 measurements per second are gathered at the rated accuracy of the balance i.e., + or - 5 x 10^{-7} grams. Over the first 300 seconds each group of 5 values is averaged and stored in memory as an averaged value every 0.1 seconds. After 300 seconds have elapsed 50 points are averaged and a value recorded every 1 second. Once 40 minutes have elapsed the values stored in memory are removed and placed in a file called CAHN.DAT on the RX02 drive. Figures 46 and 47 show the current to torque transducer section and pneumatic section of the Cahn balance. Extensive software support to utilize the data accumulated in the procedure will be presented in the Result section on the Cahn Balance system.

4) Computerized Micropilot Plant Reactor

A fully computerized laboratory scale micropilot plant reactor system was developed to provide evaluation of catalytic behavior under widely variant operating conditions. The reactor system was designed to evaluate bifunctional transition metal zeolite catalysts in the conversion of synthesis gas to gasoline. The reactor system provides for the variation of operating conditions including reactor pressure, reactor temperature, feed composition, and reactant space velocity. The entire product spectrum is analyzed by on-line gas chromatographic analysis using an internal standard, Argon. Reactor control is established through analog to digital, digital to analog, and RS232C interfaces with the LSI-11/23. A schematic diagram of the reactor system is shown in Figure 48 .

To describe the operation of this micropilot plant we will begin with the feeds to the reactor, trace the flow path through the reactor, and conclude with a discussion of the analysis procedure. Carbon monoxide, hydrogen, and argon gas cylinders supply the feed stream to the reactor. Velocity check valves were installed on the carbon monoxide and hydrogen cylinders immediately following the single stage pressure regulators. The three gas cylinders are connected via Swagelok fittings. The second stage of

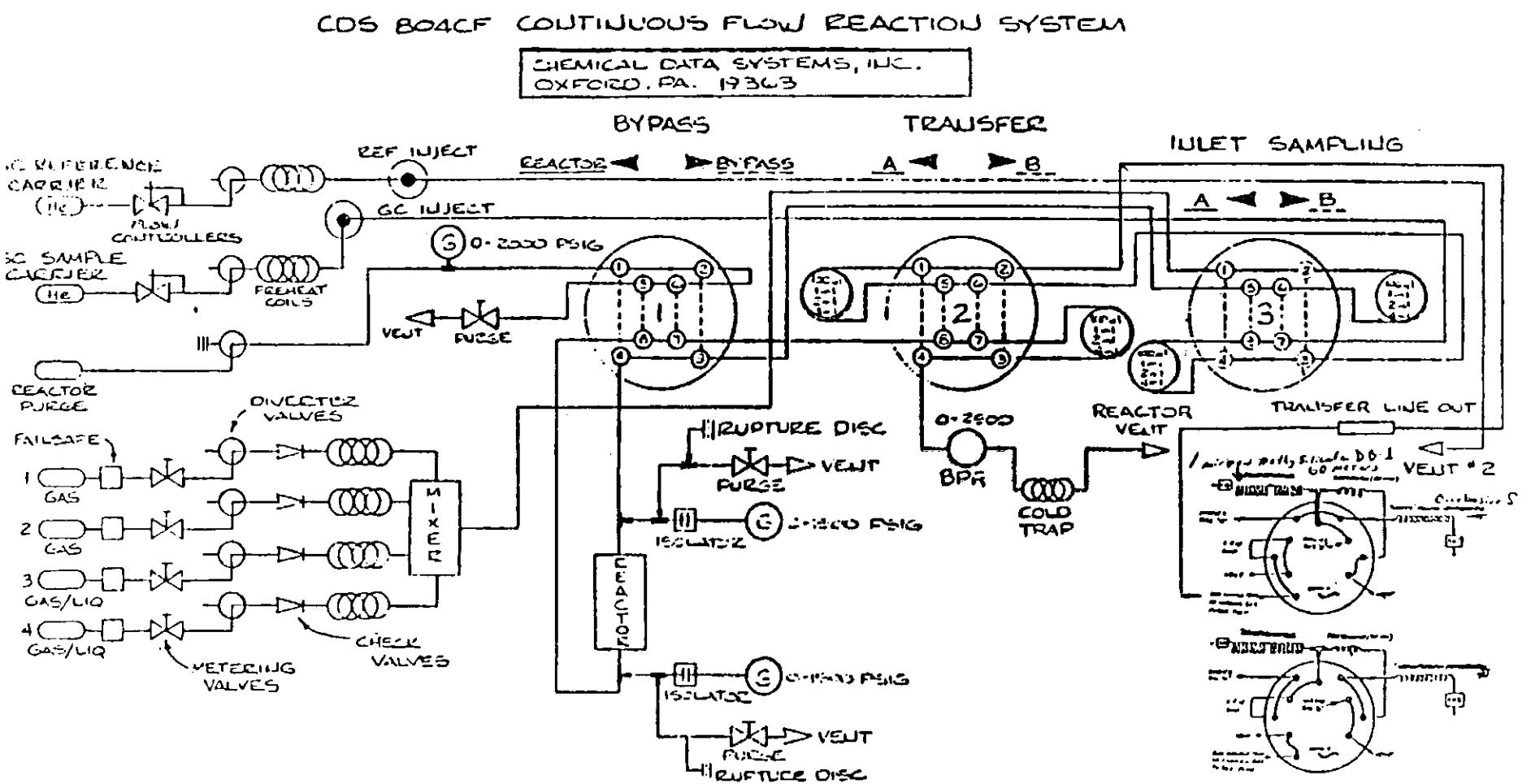

Figure 48. Schematic Diagram of Reactor System

pressure regulation is accomplished on the reactor feed control panel using GO pressure reduction regulators. The output pressure from this second stage of pressure reduction are measured using 0 to 600 PSIG Ashcroft Duragauges. The three feed streams are shown on the reactor feed control panel shown in Figure 49. Following the GC regulators each stream enters a 7 micron filter to remove particulate matter which could damage the mass flow controllers. Each stream then enters Brook's model 5850 mass flow controller. In conjunction with the LSI-11/23, the Brook's valves can adjust the mass flow rate of each feed gas by keyboard or program command in the LSI-11/23. Within each Brook's mass flow controller a precision power supply and electrical resistence heater directs a constant heat supply to the mid-point of the sensor tube carrying the gas flow. As is shown in Figure 50 resistance temperature-measuring elements are placed at equal distances upstream and downstream from the electrical resistance heater. When the gas flow velocity is 0 an equal amount of heat reaches the upstream and downstream temperature sensors labelled T_1 and T_2 in Figure 50 . When gas is flowing through the sensor tube heat is removed from the upstream temperature sensor, T_1, and from the electrical resistence heater and moved downstream to temperature sensor T_2. An increasing temperature difference develops between the two sensing elements and this difference is directly proportional to the amount of gas flowing or

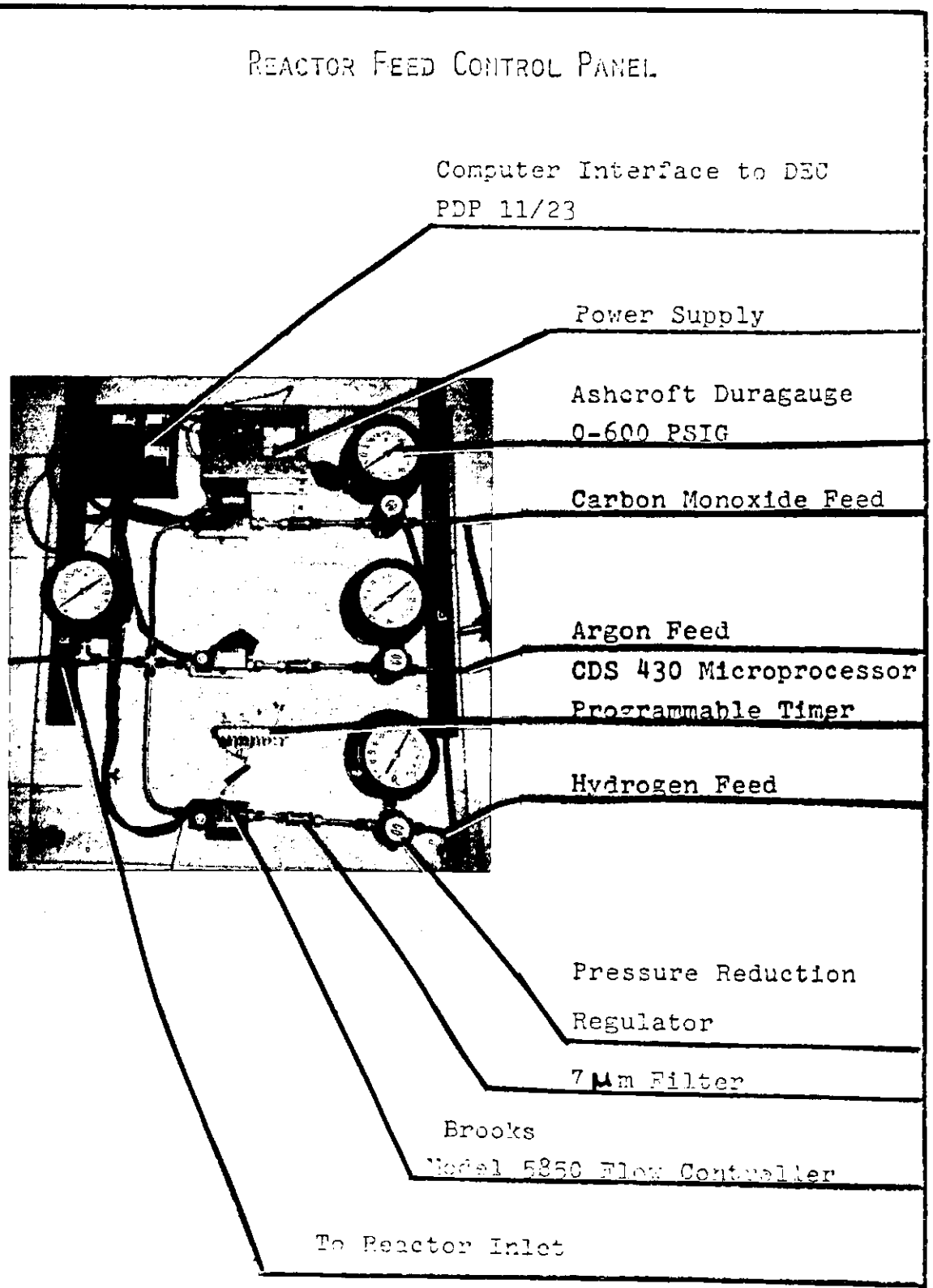

Figure 49. Reactor Feed Control Panel

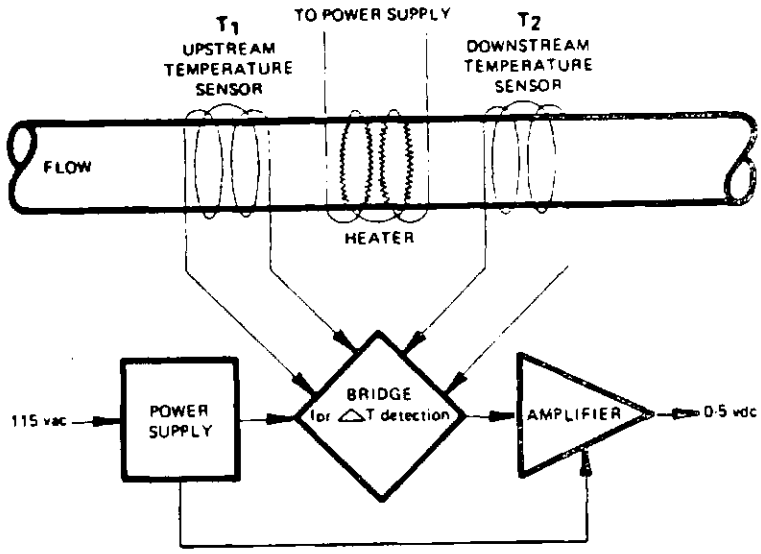

Figure 50. Brooks Mass Flow Controller

the mass flow rate. The temperature difference is interpreted by a resistence bridge circuit and an operational amplifier provides output in the range 0 to 5 volts DC to the indicating meters and to channels 1, 2, and 3 of the analog to digital converter for CO, H_2, Ar feeds, respectively. Three analog input signals provide the voltage levels the circuit attempts to match with the aforementioned analog output signals. Each mass flow controller was calibrated at the factory in accordance with the heat capacity of each of the three feed gases to provide a constant mass flow rate equivalent to the volumetric flow rate of 0 to 50 standard cubic centimeters per minute. When the digital to analog converter channels 0, 1, and 2 (for the CO, H_2, Ar feeds respectively) produce an analog voltage in the range 0 to 5 volts DC, the solenoid control valve opens or closes until

the output voltage of the operational amplifier is within 0.2% of the input voltage. When this occurs the gas flow rate is within 0.01 standard cubic centimeters per minute of the desired flow rate. Application of 0 volts DC input causes no gas to flow and application of 5 volts DC input produces a flow rate of 50 sccm. The flow rate produced is linear with the voltage applied over the 0 to 5 volt DC range. To function properly a pressure differential of 15 to 50 PSIG must be maintained. If for some reason this pressure difference is not maintained, the output of the operational amplifier will be a voltage higher or lower than the analog input voltage. The digital to analog converter therefore, creates a set point for each gas flow rate and the analog to digital converter determines how accurately the Brooks mass flow control system could effect the desired flow rate. The Ashcroft Duragauge on the left-hand downstream side of the feed control panel can be observed in conjunction with the three Ashcroft gauges on the upstream side to insure a pressure differential of 15 to 50 PSIG is maintained across each of the three mass flow controllers.

Following the feed control panel the merged gas streams enter reactant channel 1 of the Chemical Data System's model 803 Continuous Flow Reactor System. From there they enter a solenoid actuated valve which is controlled by the fail-safe system to be described later. The flow then enters a check valve which prevents gas flow in the direction of the feed control panel. A feed stream then enters a preheater diffu-

sion coil and mixer where it is directed to the inlet sampling vavle. The inlet sampling vavle is one of three solenoid actuated valves within the reactor valve oven. When actuated the inlet sampling valve directs a 2 cc sample of the feed stream through a heated transfer line to the valve oven in the gas chromatograph for chromatographic analysis. The feed stream then enters a solenoid controlled reactor bypass valve. From this valve it is directed to the top fed open tubular reactor where the feed is returned as product to the reactor bypass valve. The purpose of the reactor bypass valve is to vent the product stream to protect the analysis section while the catalyst is being reduced. The product stream leaving the reactor bypass valve enters the product transfer valve from which it leaves the reactor through a back pressure regulator toward the reactor vent. The product transfer valve when actuated sends a 2 cc sample of the product through the heated transfer line to the valve oven in the gas chromatograph.

a) On Line Analysis

The heated transfer line from the reactor system is a low volume capillary bore steel tube. This transfer line is continuously cleansed with a helium carrier at a flow rate of approximately 1 cc per minute. When either the inlet or product sampling valve in the reactor oven is actuated a 2 cc sample of gas explodes from reactor pressure to ambient pressure in the heated transfer line. This gas sample enters Port 1 of the 10 Port valve in the GC valve oven. As shown in Figure 51 the product sample exits Port 3 of the 10 Port valve flushing a 0.5 cc loop where it re-enters the valve at Port 4 and exists at Port 2 to vent. 1.5 seconds after the valve in the reactor oven fills the 0.5 cc loop of the GC valve a program executing in the Sigma 1B microprocessor rotates this GC valve to the position shown in analysis flow sequence B shown in Figure 52. The gas sample contained in the 0.5 cc loop is flushed by carrier A through Port 6 where it is split into 2 streams by a suagelok T fitting. Part of the sample enters column 1, which is a 3 foot by 1/8 inch packed column containing OV101 on Chromosorb W. The remainder of the product stream enters a 50 foot by 0.5 millimeter support coated open tubular column containing DC-550 liquid phase. After a

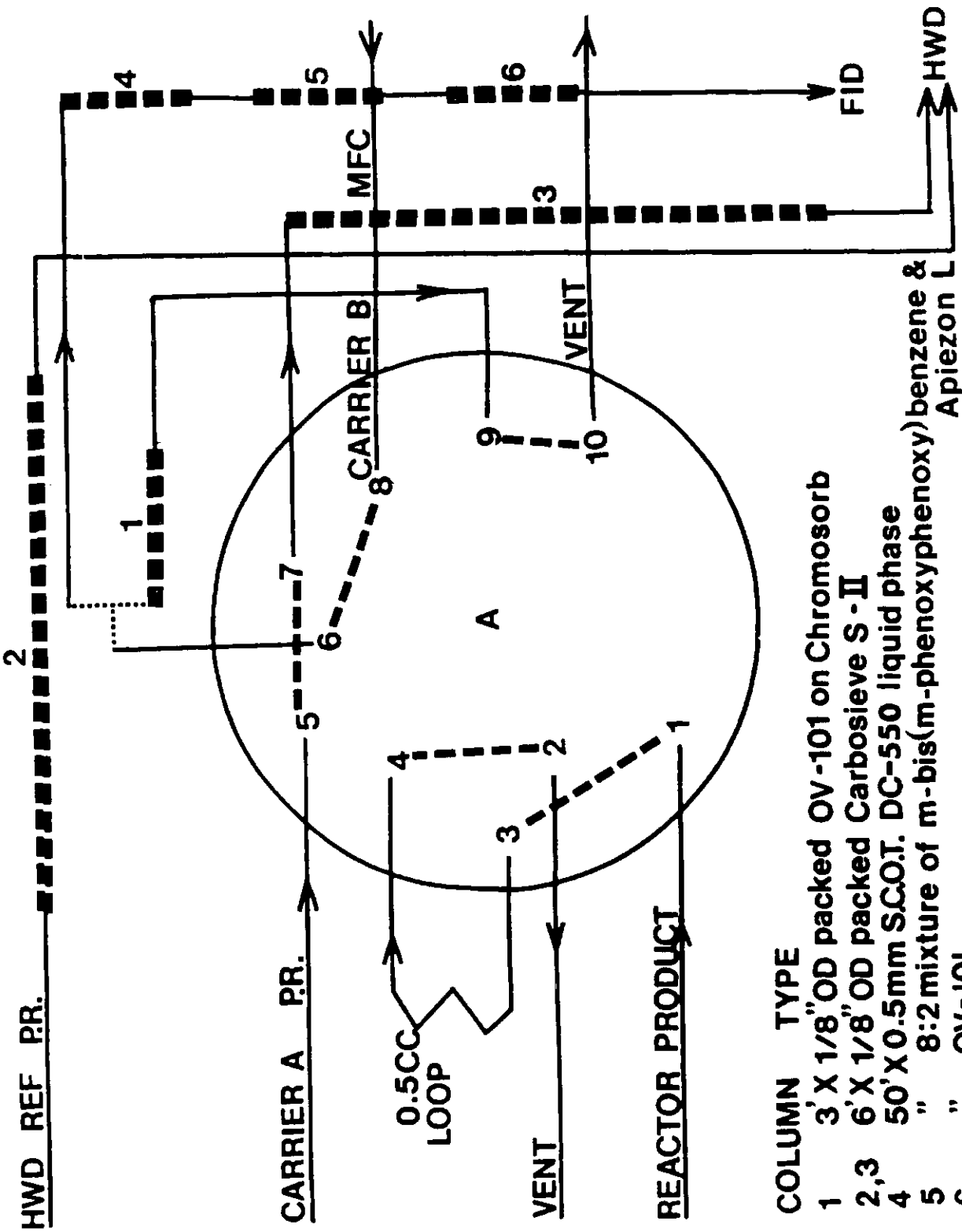

Figure 51. Analysis Flow Sequence A

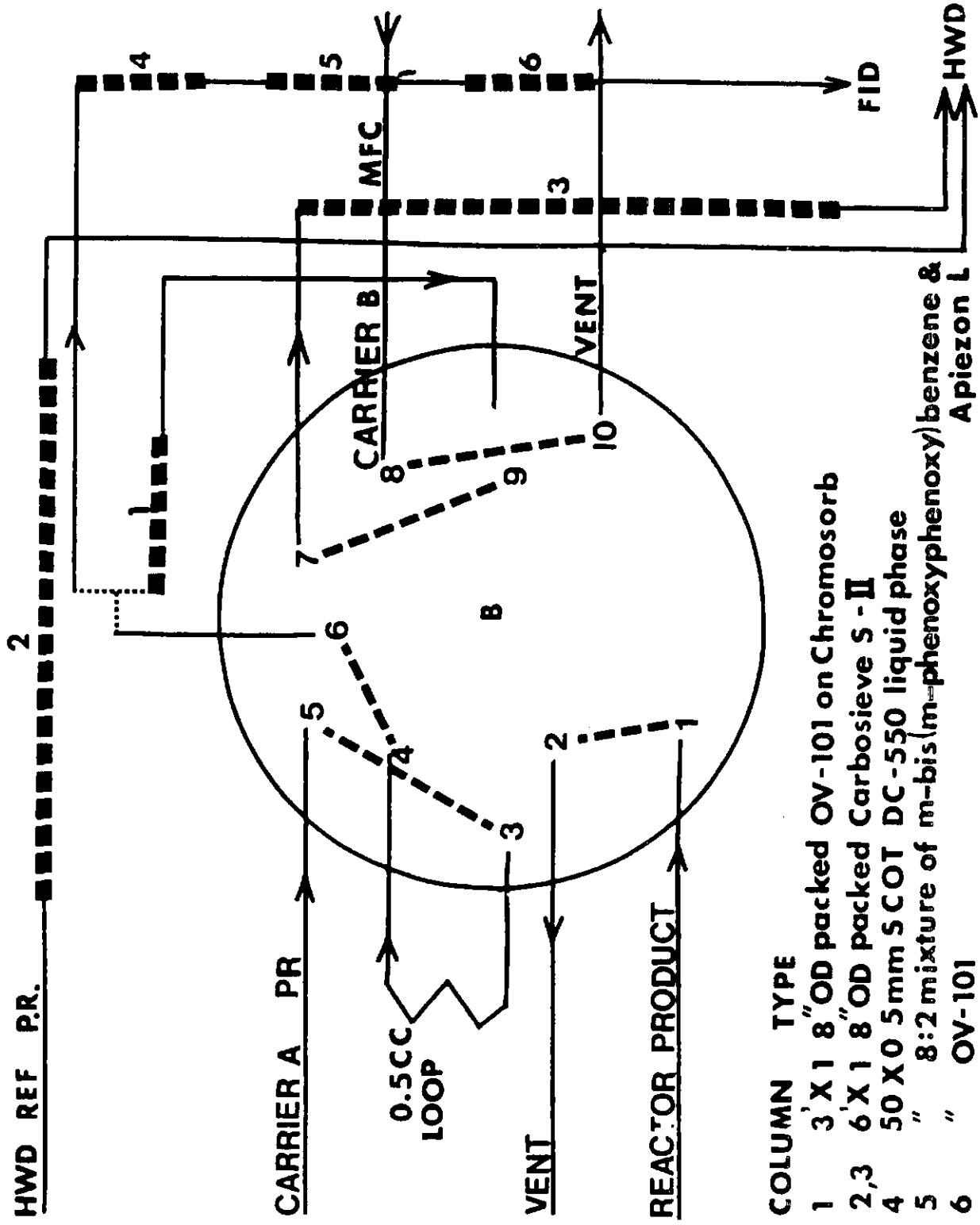

Figure 52. Analysis Flow Sequence B

programmed length of time, approximately 45 seconds, hydrogen, argon, carbon monoxide, water, carbon dioxide, methane, ethyne, ethylene, and ethane elude column 1 shown in Figure 52 and are flushed through Ports 9 and 7 into column 3. Column 3 is a 6 foot by 1/8 inch packed column containing Carbosieve S-2 which is used to separate the permanent gases. Immediately following the ellusion of ethane from column 1 and before propylene eludes this column, the program in execution in the Sigma 1B microprocessor rotates the 10 Port valve to the position shown by analysis flow sequence A shown in Figure 51 In this position a temperature programmed sequence raises the temperature in the GC column oven from -50 C to 150 C at 6 C per minute. The valve oven then isotherms at 150 C for 20 minutes. During this period carrier A pushes the permanent gases, i.e., hydrogen through ethane through the hot wire detector. The reference carrier for the hot wire detector passes through column 2 which is equivalent to column 3 which is also in the GC valve oven. As the flow rate of carrier A increases due to the expansion of the gas contained in column 3, the flow rate to the reference side of the thermoconductivity detector similarly increases due to the expansion of the gas in the identical column 2. The baseline of the thermoconductivity detector is thereby maintained relatively stable over the entire course of the temperature program.

Simultaneously, carrier B exits Port 6 shown in Figure 31, is split at the Swagelok T and provides the carrier for the flame ionization detector. The entire product spectrum from methane through C_{16} is separated by the three support coated open tubular columns which are in series. These support coated open tubular columns labelled 4,5, and 6 in Figure 51 are coated with three different phases described in the legend of Figure 51. Simultaneously, the C_2^+ fraction contained in column 1 is carried by carrier B through Ports 9 and 10 to vent.

Although, other authors[166,167,168] have attempted similar analyses using wall-coated, open tubular columns, packed columns, and support-coated, open tubular columns, the method herein described is the first time this most complex analysis has been performed using a single 10 Port valve. There are many advantages to this approach, the most important of which will be discussed.

The product stream is not continuously sent through the heated transfer line to the analysis section. The heated transfer line is filled with product only immediately before the analysis is to take place. This prevents condensation of large amounts of the heavier hydrocarbon oils and waxes within the transfer line which can lead to plugging of the transfer line or to erroneous analyses showing higher concentrations of the higher boiling point products. A second advantage is that the same transfer line and analysis system

can be used for the analysis of the feed stream. The analysis section performs equally well whether the transfer line is filled by the feed valve or the product valve within the reactor valve oven. Further, since the majority of costs of implementing this reactor system were directed at the production of the Analysis section, multiplexing the Analysis section across many reactors is advantageous. If the budget permitted, a dozen microreactors could share the Analysis section providing the LSI-11/23 and Sigma 1B computers sequenced which reactor filled the transfer line for a particular analysis period. Since testing these bifunctional catalysts involves days of waiting for the reduction, carbiding, and approach to steady state the Analysis section remains idle for the vast majority of the time. Cascading the reactors and multiplexing their output to the Analysis section is, therefore, an economic incentive.

The physical lay-out of components in the micropilot plant reactor is shown in Figure 53. Because of the explosiveness and toxicity of the feed gases in this reaction, measures were undertaken to safeguard the reactor system. The CDS Fail-safe unit continuously monitors all heated zones within the reactor testing for over-temperature conditions and for discontinuity or short in a thermocouple. The Fail-safe unit also tests for a power failure in the reactor which is extremely important in this reaction. In the event of a power failure the reactor begins to cool and

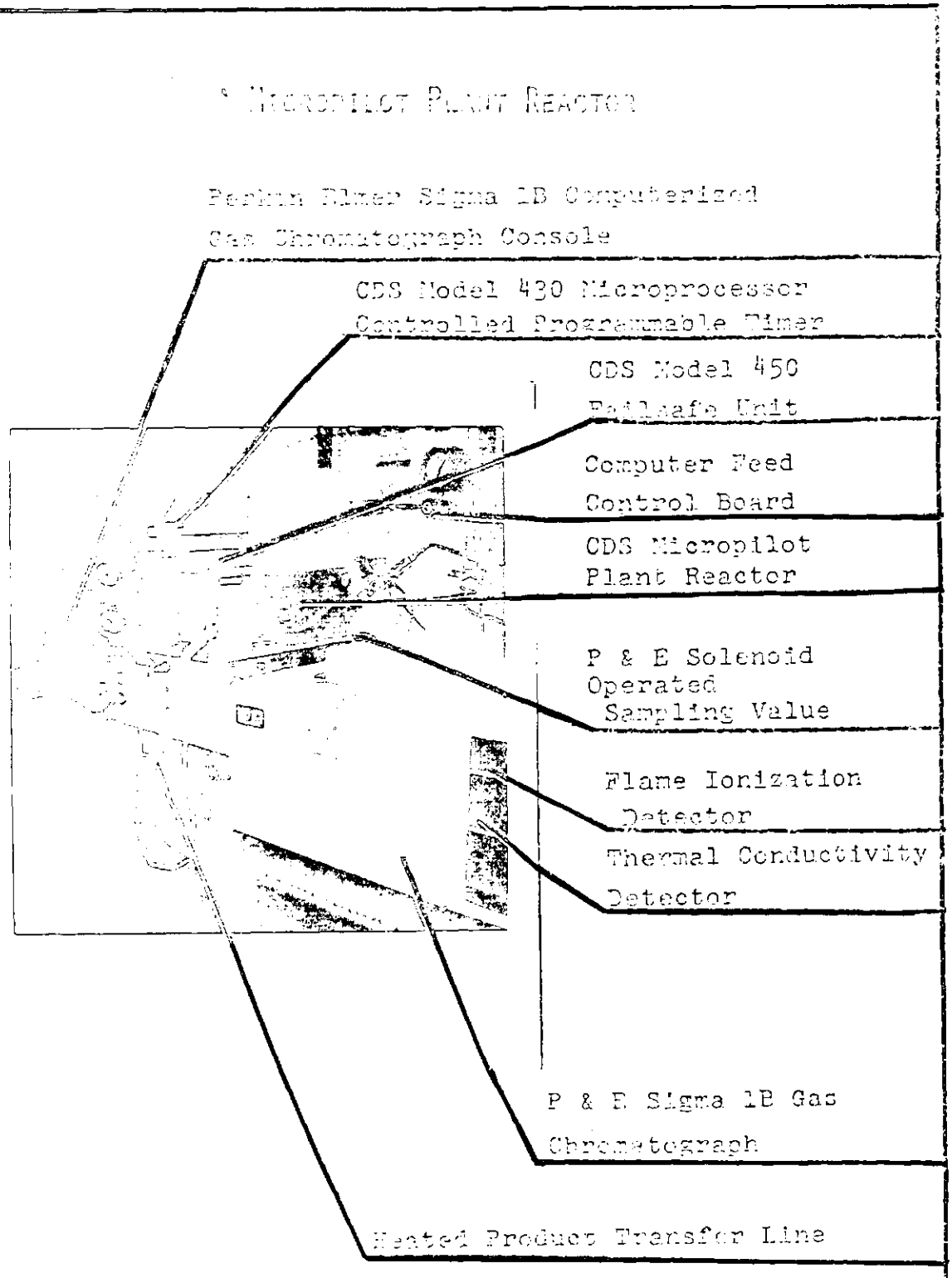

Figure 53. Micropilot Plant Reactor

at approximately 140 - 150 C the carbon monoxide reacts with the steel shelf of the reactor and produces iron carbonele. Iron carbonele is considerably more toxic than the reactants and its formation also weakens the reactor itself by removing iron. The Fail-safe unit responds immediately upon the detection of a system malfunction by shutting off the feed stream through a solenoid control valve, shutting off all heated zones in the reactor, and purging the reactor with a helium stream to prevent the formation of iron carbonyl.

The final necessary safeguard was to provide a means by which the LSI-11/23 could determine if the reactor began to leak hydrogen or carbon monoxide and to notify the operator if this occurred on a 24 hour per day basis. Since for the majority of the day the reactor is being run unattended and because a carbon monoxide level of only 800 parts per million can be fatal in one hour, a breach in the reactor integrity was of paramount concern. General Electric Corporation donated to Worcester Polytechnic Institute a direct reading carbon monoxide detector model 15ECS3C01. This device was interfaced with the LSI-11/23 through channel 7 of the analog to digital converter. A schematic of this device is shown in Figure 54. Using a semipermeable teflon membrane, carbon monoxide is measured through the current resulting from its electrochemical oxidation. A signal is amplified for visual crystal read-out on the top of the

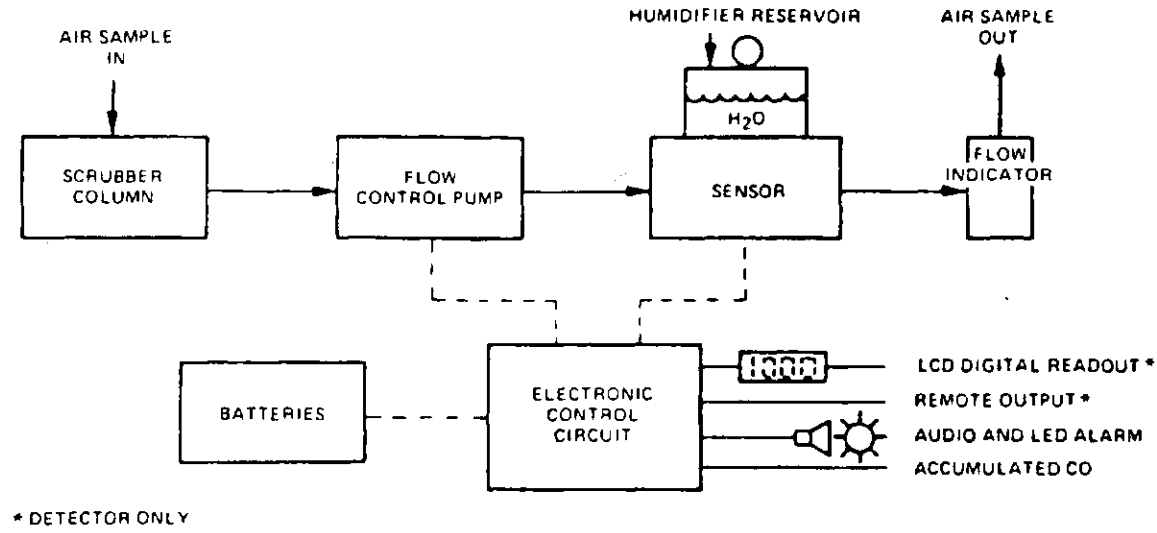

Figure 54. General Electric Corporation Direct Reading Carbon Monoxide Detector Schematic

device and an audible alarm is set to go off within the device if the ambient carbon monoxide concentration exceeds 200 parts per million. The analog output of this device which is normally used for chart recording enables the LSI-11/23 through its analog to digital converter to con-

tinuously monitor the carbon monoxide concentration. If the concentration of carbon monoxide exceeds 50 parts per million the LSI-11/23 shuts off the hydrogen and carbon monoxide feeds by zeroing the output voltage in channels 0 and 1 of the anlog to digital converter. It then increases the argon feed rate to its maximum of 50 sccm and causes operational state 8 to be invoked on the Cahn balance interface control panel. This shuts off the Cahn balance and shorts the leads to the Heath Kit autodialer which then proceeds to telephone the number which is set by slide switches on the front panel of the autodialer. If the telephone number is busy or a no answer signal is received the autodialer will continue to poke the telephone exchange until its message is sent. The message from the autodialer is not voice but a sequence of tones and is, therefore, only intelligible by someone who has been trained to recognize the tones. Because the feed gases are merged immediately following the feed control panel it was not necessary to simultaneously monitor ambient hydrogen concentrations. If hydrogen began to leak, carbon monoxide would also be escaping. The importance of shutting off the Cahn balance is to prevent its programmable oven from igniting the escaping carbon monoxide or hydrogen gases.

5) Computerized X-Ray Diffraction Facility

The Norelco XRG 300 X-ray diffractometer available to this project was a manually operated unit which presented the intensity, 2 theta information on a strip chart recorder. The inherent inaccuracy in estimating the 2 theta angle at which intensity maximized coupled with the tremendous thruput expected from this diffractometer made the computerization of its operation and computer work-up of the accumulated data a desired goal. Three devices manufactured by Norelco Philips were added to the diffractometer to automate the control of this device. An angle mode programmer, a scaler-timer, and an output interface automated the control of the diffractometer and presented for data output serial ASKII at 300 baud and 60 mA active. To make this output form compatible with input to the PDP-20 a 60 mA active to 20 mA passive converter was added followed by a 20 mA passive to EIARS232-C. The RS232 signal was compatible with a computrend modum which served to transfer the intensity 2 theta tupules to the PDP-20. To make the diffractometer compatible with the LSI-11/23, the 20 mA passive signal is converted to RS232-C by way of a DLV11-KA which is connected to a channel on the DLV11-J asynchronous serial line interface. The extensive software support for the x-ray diffraction system in both the PDP-20 and LSI-11/23 computer systems will be described in the Results section on the x-ray diffraction system. The integrated zeolite research laboratory described in the previous sections is shown in Figures 55 and 56 .

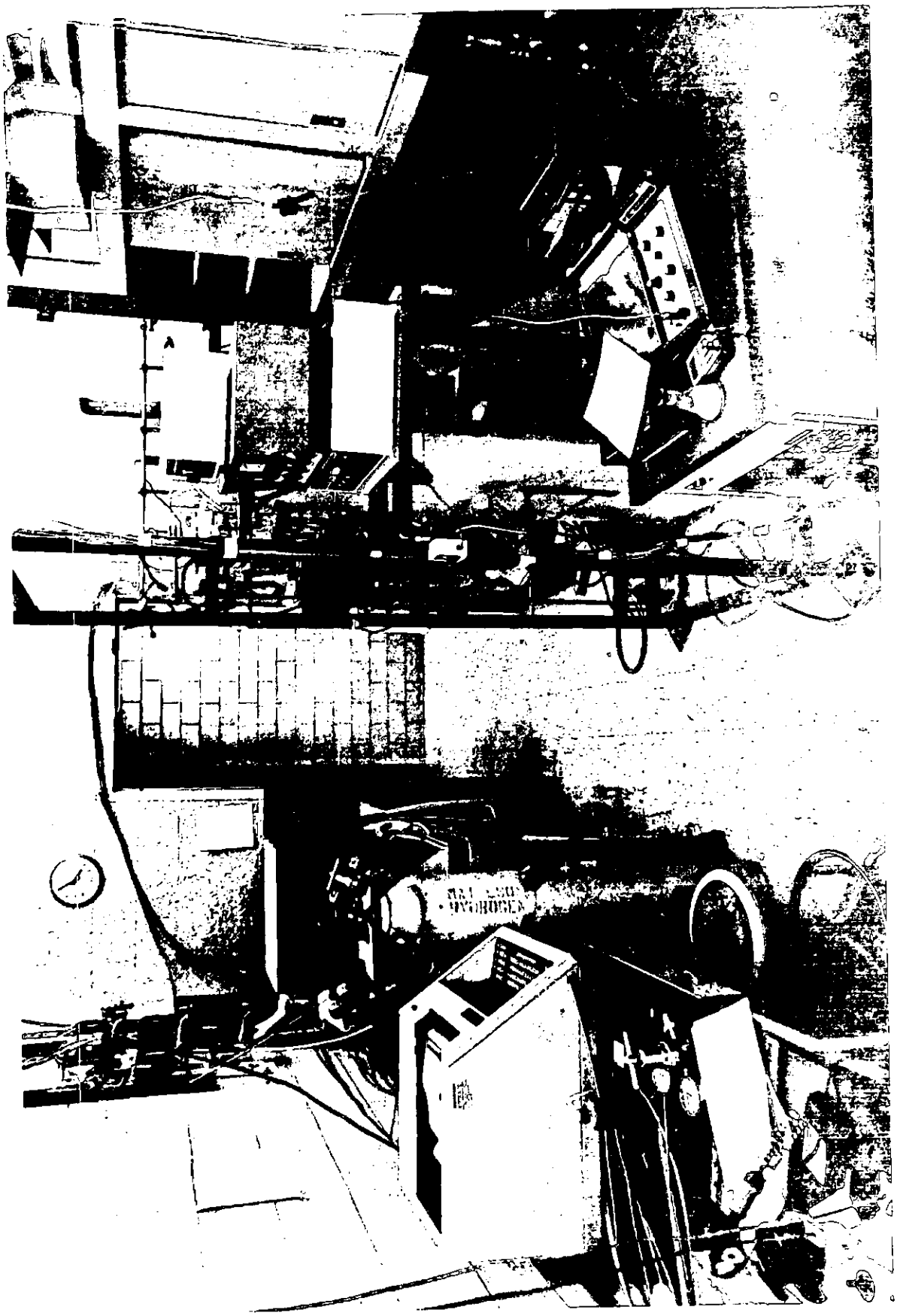

Figure 55. Integrated Zeolite Research Laboratory

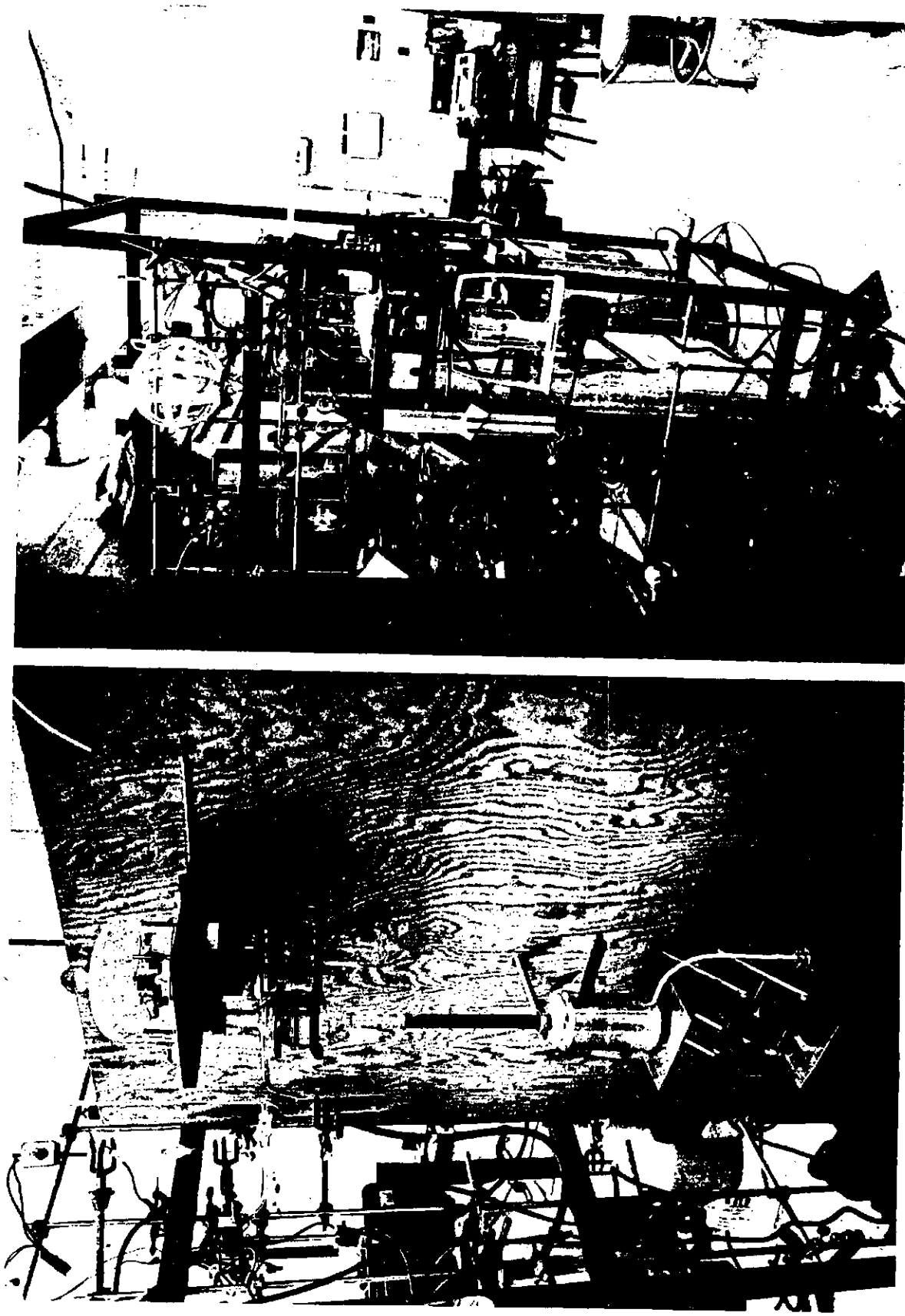

Figure 56. Integrated Zeolite Research Laboratory