3. Bifunctional Transition Metal-Zeolite Catalysts

Bifunctional transition metal-zeolite catalysts are capable of converting synthesis gas to gasoline in a single reaction step for they contain both the CO reduction function and the hydrocarbon synthesis function. In the MTG technology the reactor employed for the synthesis of methanol from synthesis gas must be operated under conditions different from those used in the dehydration and hydrocarbon synthesis reactors. The reasons for this are the thermodynamics involved in methanol synthesis, the fact that traditional methanol synthesis catalysts are destroyed at the high reaction temperatures required for good ZSM-5 activity, and the fact that compressor costs would be prohibitive if methanol was to be synthesized at the temperatures required for good ZSM-5 activity. The thermodynamics of methanol synthesis were reviewed by Strelzoff[161] and Thomas et al.[162] The variation of equilibrium methanol content as a function of pressure and synthesis gas ratio at 350 C is shown in Table 22.[161] From this table it can be observed that at a temperature of 350 C and a pressure of 50 atms., the equilibrium mixture of carbon monoxide, hydrogen, water and methanol would contain only 2.z2 and 2.3 mole% methanol for 1:1 and 2:1 syngas ratios. At this temperature we would be required to pressurize 2:1 syngas to 500 atms. to effect an equilibrium

Pressure atm.	H_2/CO Molar Ratio					
	9:1	4:1	2:1	1:1	1:2	1:4
50	1.5	2.2	2.3	2.3	1.5	0.7
75	2.5	4.1	5.1	4.1	2.5	1.2
100	3.9	6.7	8.4	6.7	3.8	1.8
125	5.2	9.4	12.1	9.5	5.4	2.5
150	6.6	12.2	15.9	12.3	6.8	3.3
175	7.5	14.6	19.7	15.2	8.2	3.0
200	8.3	17.4	23.4	19.0	9.6	4.4
250	9.6	21.4	30.8	22.2	11.9	5.7
300	10.7	24.2	37.8	26.5	13.6	6.3
350	11.3	26.2	44.6	29.8	15.5	7.5
400	11.5	27.8	51.4	32.3	15.8	7.9
450	11.8	29.4	57.6	34.5	17.7	8.4
500	12.0	30.7	63.5	36.5	18.5	8.9

Table 22. Equilibrium Methanol Content in Mole Percent in the Reaction Mixture From Inlet Gas Mixtures of Various Hydrogen Carbon Monoxide Molar Ratios.[161]

conversion to 63.5 mole % methanol. The equilibrium concentration of methanol in this reaction increases with pressure and decreases with temperature. For economic considerations, it is desirable to synthesize methanol at low temperatures such that the required pressure necessary to effect a chosen conversion will be low. If, however, methanol is synthesized on a bifunctional catalyst it can be immediately converted by the zeolite portion to dimethyl ether and higher hydrocarbons. The concentration of methanol over the methanol synthesis function is, therefore, lowered and the synthesis gas to methanol reaction driven to the right. The overall reaction mechanism involved is shown in Figure 37.[163]

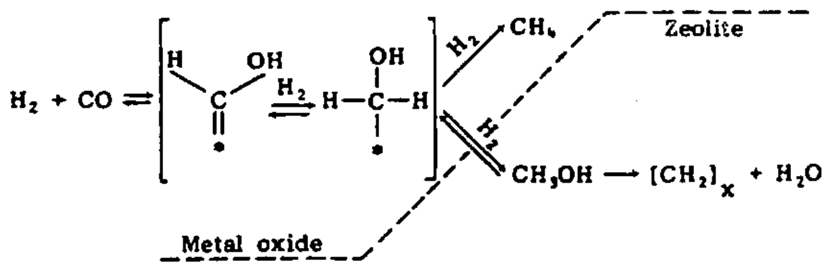


Figure 37. Reaction Mechanism of Methanol over the Methanol Synthesis Function.[163]

First methanol is synthesized on a transition metal or transition metal oxide. The methanol formed contacts the zeolitic surface where it is transformed through dimethyl ether to higher hydrocarbons. This drain-off mechanism reduces the overall cost of the MTG process for the steps which require three reactors in this process are accomplished in a single reactor via dual function catalysts. Further, the compressor cost necessary in the methanol synthesis step in the MTG technology can be substantially reduced for it is no longer necessary to achieve high pressure if methanol is being drained off as rapidly as it is formed. The utilization of the approach is only delayed by the development of a long-life, highly active bifunctional catalyst demonstrating good selectivity to gasoline range hydrocarbons. The obvious process advantage and economic advantage of the STG approach over all previous technologies including MTG made the development of the aforementioned bifunctional catalyst the paramount concern in this investigation.

III. Experimental Methods

Integrated Zeolite Research Laboratory

To facilitate the evaluation of the efficacy of bifunctional transition metal zeolite catalysts in the synthesis of gasoline range hydrocarbons from synthesis gas, an integrated computerized zeolite laboratory was designed and implemented. For the qualitative and quantitative determination of the zeolite and other phases hydrothermally synthesized, a Norelco XRG 3000 x-ray diffraction unit was automated such that it could communicate with PDP-20 and/or LSI 11/23 computer systems. To evaluate the sorbtion characteristics of bifunctional zeolite catalysts, i.e., sorption rate, extent of adsorption, adsorption isotherms etc., a Cahn 1000 balance system was integrated with an LSI 11/23 computer system. To determine the extent of CO conversion, the extent of hydrogen conversion and the hydrocarbon fraction of product in each carbon number range, a micropilot plant reactor system was interfaced with Perkin-Elmer Sigma 1B and DEC LSI 11/23 computer systems. To provide for graphical output of the data accumulated by the aforementioned systems the LSI 11/23 was interfaced with a Tektronix 4006-1 Graphics Terminal and a Tektronix 4662 interactive digital plotter. To monitor ambient carbon monoxide concentrations within this laboratory

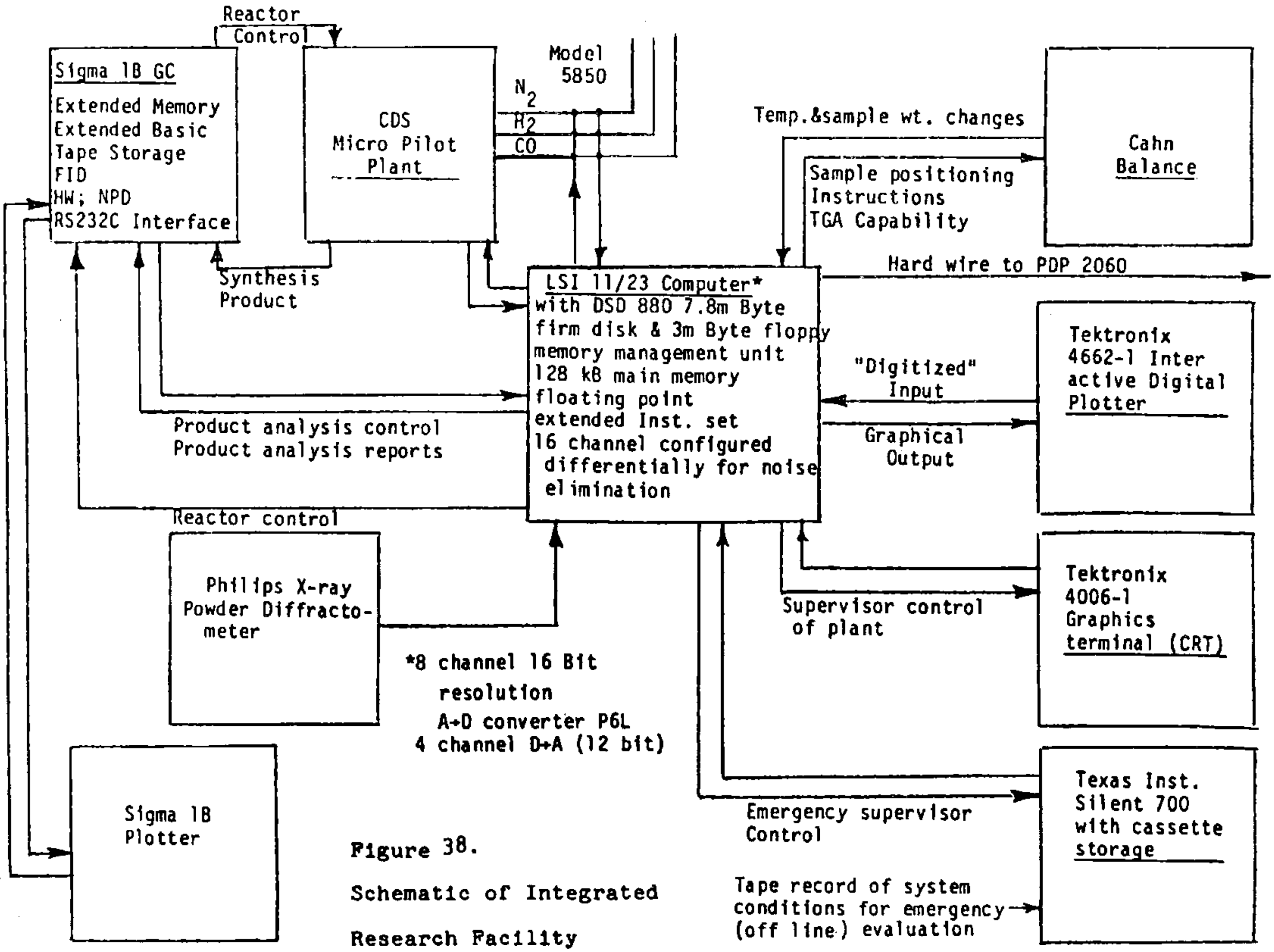


Figure 38.

Schematic of Integrated Research Facility

and to effect an emergency telephone call in the event of crisis, the LSI 11/23 system was interfaced with a General Electric model 15ECS3C01 direct reading carbon monoxide detector and a Heath Kit autodialer. An overall schematic of this integrated research facility is shown in Figure 38. This Figure presents an overview of the communications architecture in this laboratory. The specific nature of the communication between the LSI 11/23 and the peripheral components will be discussed in detail. As the heart of this micropilot plant design is the LSI 11/23 computer system we will begin this section with a description of this computer.

1) The LSI-11/23 Computer

The capabilities and versatility of the LSI 11 family computers have made them extremely popular for process control applications. Manually operated process control systems are rapidly being replaced with cost effective LSI 11s and over 100,000 LSI 11 family microcomputers are in world-wide use today. The LSI 11 computer system is built around a back plane known as a Q-Bus. All communications between the LSI 11 micrcomputer module random access memory and the peripheral devices is transmitted through the Q-Bus. A major advantage of the LSI 11 family is that a wide variety of peripheral devices and interfaces are supported by the Q-Bus architecture. The typical LSI 11 system configuration is shown in Figure 39.[164] All modules connected to this common LSI 11 Bus system receive the same interface signals from the Bus. The Bus provides for vector priority interrupts, programmed I/O transfers, and direct memory access I/O data transfers.

The PDP 11 instruction set contains more than 70 operations and utilizes an extremely versatile set of addressing modes. The eight addressing modes it supports include register, register-deferred, auto increment, auto increment deferred, auto decrement, auto decrement deferred, index, and index deferred. Memory organization in the LSI 11

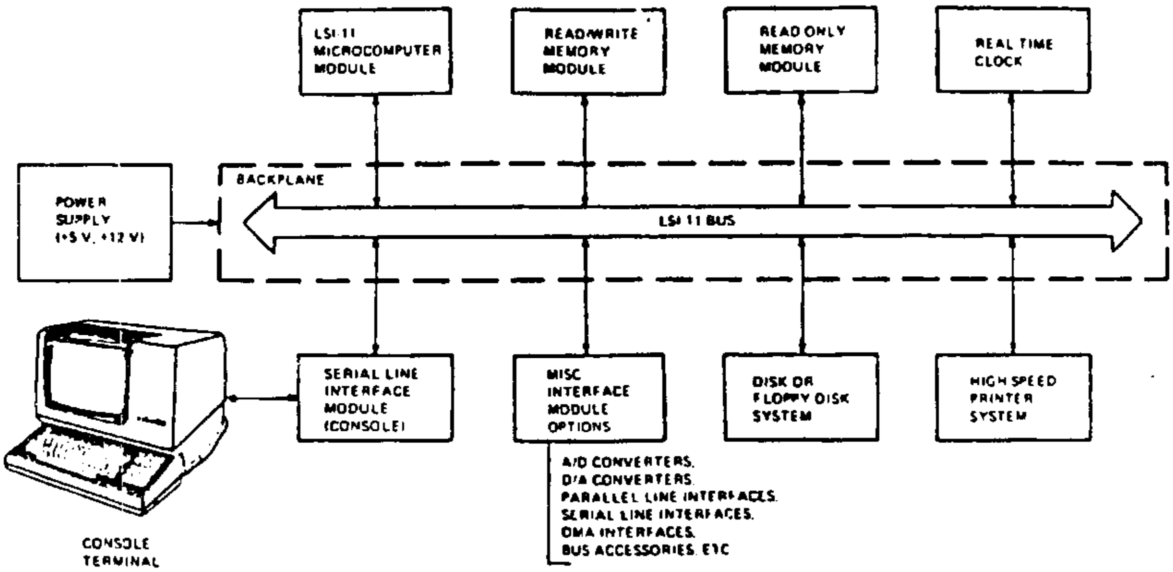


Figure 39. Typical LSI-11 System Configuration.[164]

is based upon 16-bit words which are divided into an 8-bit low byte and an 8-bit high byte. Instructions exist within the LSI-11 instruction set which provide acess to the low or high byte and to the entire 16-bit world. Octal (base 8) is used for address locations, contents of addresses, and an instruction operation code. 64 thousand bytes of memory are available in the direct address space. The organization of this direct access space is shown in

Figure 40 [164] The LSI 11/23 computer system provides for a maximum random access memory size of 256 thousand bytes.

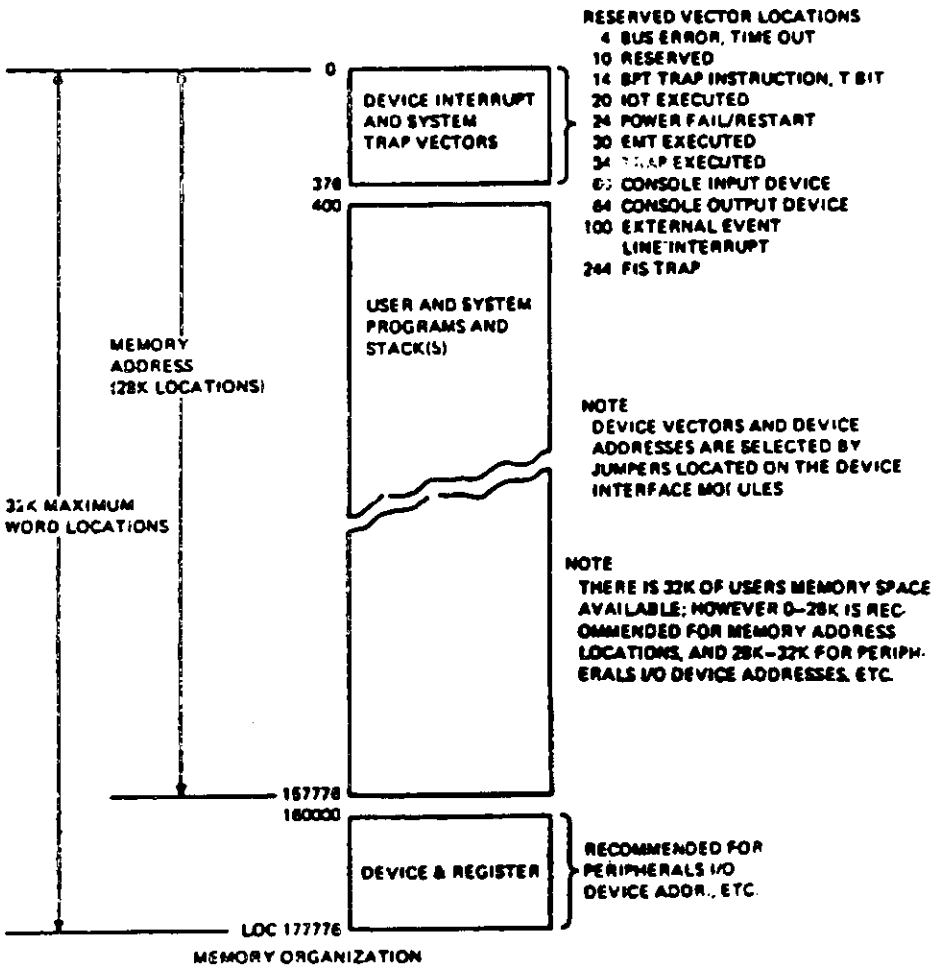


Figure 40 . Memory Organization [164]

This is accomplished by extending the 16-bit physical word size to 18-bits. The 256 thousand bytes are subdivided into four pages containing 64 thousand bytes each. The memory management unit utilizes the highest 2 bits to determine in which of the four aforementioned pages the memory location to be accessed resides. The memory management unit, therefore, labels the four pages in accordance to whether the 17 and 18-bit is 00 (for the base direct access portion of memory or 01, 10, or 11 for the three virtual pages of physical memory). In addition to the random access memory, eight 16-bit general purpose registers reside in the central processor module. Of these 8 general purpose registers which are labelled R0 through R7, two have specific functions. In the LSI-11 instruction set R7 serves as a program counter which keeps track of the instruction within a program which is to be executed. R6 serves as a stack pointer which contains the address of the last memory location used in the temporary memory space known as the stack. Registers R0 through R5 have a multitude of uses and can serve as accumulators, index registers, auto increment registers, auto decrement registers, arithmetic operations, etc. Another 16-bit register contained in the central processor module is the processor status word. The processor status word contains information relevant to the current processor status. The information contained in the PSW includes the current processor priority, the conditions codes which describe the arithmetic and logic results of the last instruction executed, and an indicator for detecting the execution of an instruction to be trapped. The aforementioned priority is of importance in assigning a priority to a program being executed or to an interrupt service routine. This can most easily be described by reiterating the sequence of events which occur when a character is typed at a terminal.

If a program is in execution in an LSI-11/23 and requires a byte of information from the operator (single askii character) two techniques can be implemented as to how the executing program can handle this need. The first is called polling. In polling the processor looks at the low byte of the memory location which receives the character from the terminal. If the character is not there, the processor goes back and looks again at this low byte. This process occurs redundantly hundreds of thousands of times a second until finally the operator types the character and the program can continue its execution. In effect what occurs, is the processor wastes CPU time for it spends its entire capacity in checking the contents of that word, therefore, no further progress on the program is made. Alternatively, the algorithm can be set up to provide for a processor interrupt when the character is finally typed. There can be many processor interrupts assigned for different priorities in the LSI-11/23. The advantage of the interrupt strategy is that the program can continue execution and not have to wait for the character to be typed or other event to occur. The higher the level of priority assigned a particular interrupt routine, the faster it will be serviced, if other interrupts are simultaneously pending. If the processor is the mother bird and the baby bird holding its head highest will be fed first. The significance of this capability in the control of chemical engineering systems cannot be over emphasized. If the processor is busy compiling data or reporting data when a crisis situation occurs it is crucial the processor stop its routine duties to immediately take care of the crisis situation such as reactor over temperature, etc. Extensive use of this interrupt handling capability was made in the design of this laboratory. In the collection of sorbtion rate data at 50 observations per second through an analog to digital converter it is imperative to use the interrupt strategy. If the processor does not remove a data value determined by the analog to digital converter and store it in a memory location on an immediate basis, by the time it goes to collect this value the value would have been replaced with a new or updated result.

Two additional options included in this LSI-11/23 system are the extended instruction set and the floating point unit. The extended instruction set contains 4 instructions that perform multiple arithmetic shifting and signed integer, multiply and divide. The floating point option contains 46 microcode instructions which perform floating point arithmetic logic and conversion and operates at a rate substantially faster than their software counterparts.

The LSI-11/23 computer system consists of a KDF11-AA LSI-11/23 central processing unit, two MSV11-DD 64 Kbytes random access memory, one KWV11-A programmable real-time clock, two DLV11-J 4-channel asynchronous serial line interface, one DSD880 disc storage system with controller, one DT-2764-DI-PGL 16-bit 8-channel differentially configured programmable gain analog to digital converter, one DT2766 4-channel 12-bit digital to analog converter, two DLV11-KA EIA to 20 mA converters, and one DT701 screw terminal conditioning panel.

The programmable real-time clock provides a means for determining time intervals or counting events. It is utilized within this laboratory to generate processor interrupts at various time intervals to synchronize events occurring in "real-time" in the "real-world" with algorithms responsible for controlling events in and accumulated data from the real-world.

The two 4-channel asynchronous serial line interfaces are used to interface various peripheral equipment to the LSI-11/23 Bus. The 8 asynchronous serial ports provided by these two boards provide the means for the Tektronix 4006-1 graphics terminal, the 4662 interactive digital plotter, the Perkin-Elmer Sigma 1B gas chromatograph console, the Norelco x-ray diffractometer, and the DEC PDP-20 to communicate through the Q-Bus to the central processing unit.

The DSD880 disc storage system is an advanced storage capability which emulates one RX02 and one RL02 DEC storage systems. This storage system contains its own microprocessor which enables off-line disc diagnostics through the hyperdiagnostic's panel and direct memory access.

The RX02 drive is capable of formatting, reading, and writing in accordance with the single density single-sided, single density double-sided, double density single-sided, or double density double-sided disc formats. The firm disc contained in the DSD880 unit is a 7.8 megabyte disc system which can be readily made to emulate a 10 megabyte RL02 disc system through minor patches to the RT11 operating system. The 2.2 megabyte difference in the drive sizes is most conveniently removed from the operating systems site through the creation of a bad file.

The DT-2764 analog to digital converter is a low-level wide-range analog input system allowing programmable gain selection of full-scale input ranges of 10 millivolts to 10 volts. This analog input device provides a means for the direct interface of low-level analog signals such as those from thermacouples without the need for external amplifiers or extensive signal conditioning. The 8 isolated differential channels contain differential amplifiers which have 4 programmable acceptable gain ranges of 1, 10, 100 and 500. Merely setting 2 bits in the control status word selects a particular gain. The input impedence of the DT2764 is 100 megohm.

The DT2766 digital to analog converter is a 4-channel 12-bit accuracy analog output system which provides 0 to +10 volts output at 20 mA. These A to D and D to A converters were used in the data acquisition and process control of the micropilot plant reactor and the Cahn Balance system. A diagram of the LSI-11/23 computer system is shown in Figure 41.

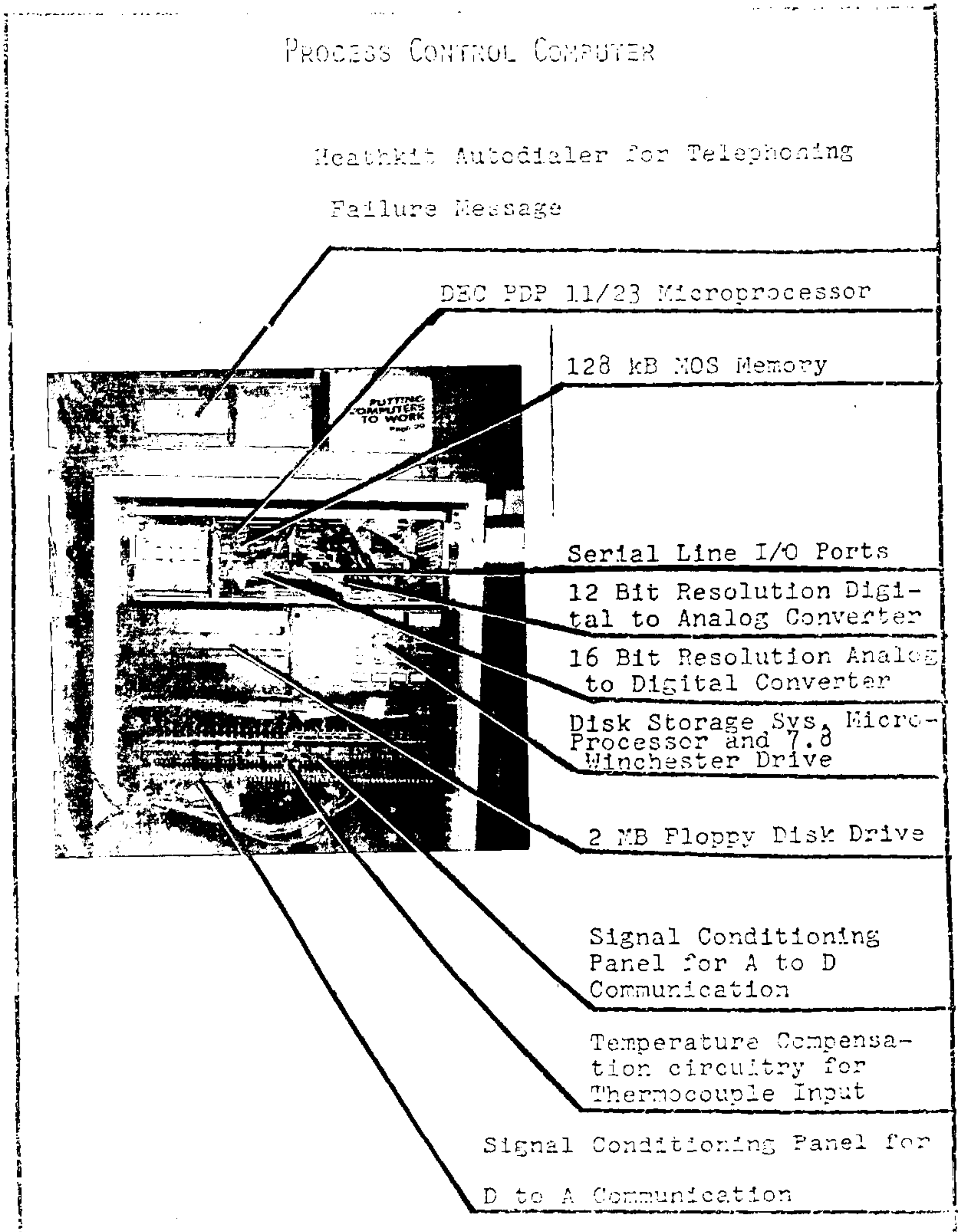


Figure 41. LSI-11/23 Computer System

CAHN Balance System - Computer Control

A Cahn 1000 electrobalance is an extremely sensitive force measurement instrument designed to measure forces up to 100 grams and detect force changes as small as 5×10^{-7} grams. The heart of the Cahn 1000 system is a current to torque transducer shown in Figure 42[165] The balance beam is suspended by a taut metallic ribbon. A photodiode sensor determines if the forces on each balance pan are equivalent. If they are not equivalent the control circuitry increases the current through a magnetic coil to introduce a magnetic field force to balance the discrepancy in forces on the balance pans. The increase in current through the coil is established by means of increasing the voltage across the coil. The change in voltage can be measured by the high resolution analog to digital converter previously described. A simple conversion factor translates the measured analog signal to the force change which is linear with it. The 16-bit resolution of the analog to digital converter provides for an accuracy better than the rates accuracy of the Cahn balance.

All communication between the Cahn balance system occurs through the analog to digital and digital to analog converters. Communication from the Cahn balance to the LSI-11/23 takes place through the analog to digital converter

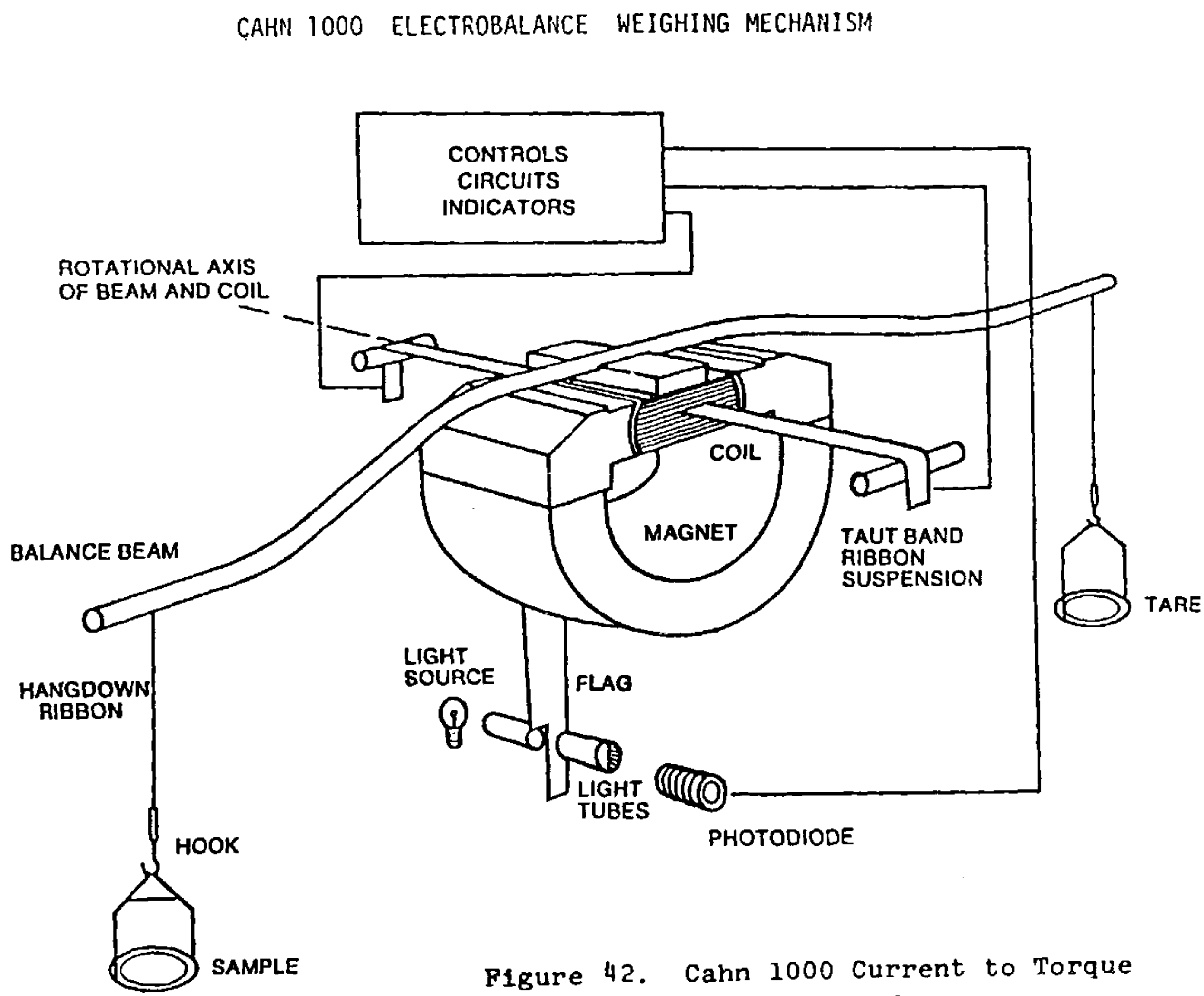
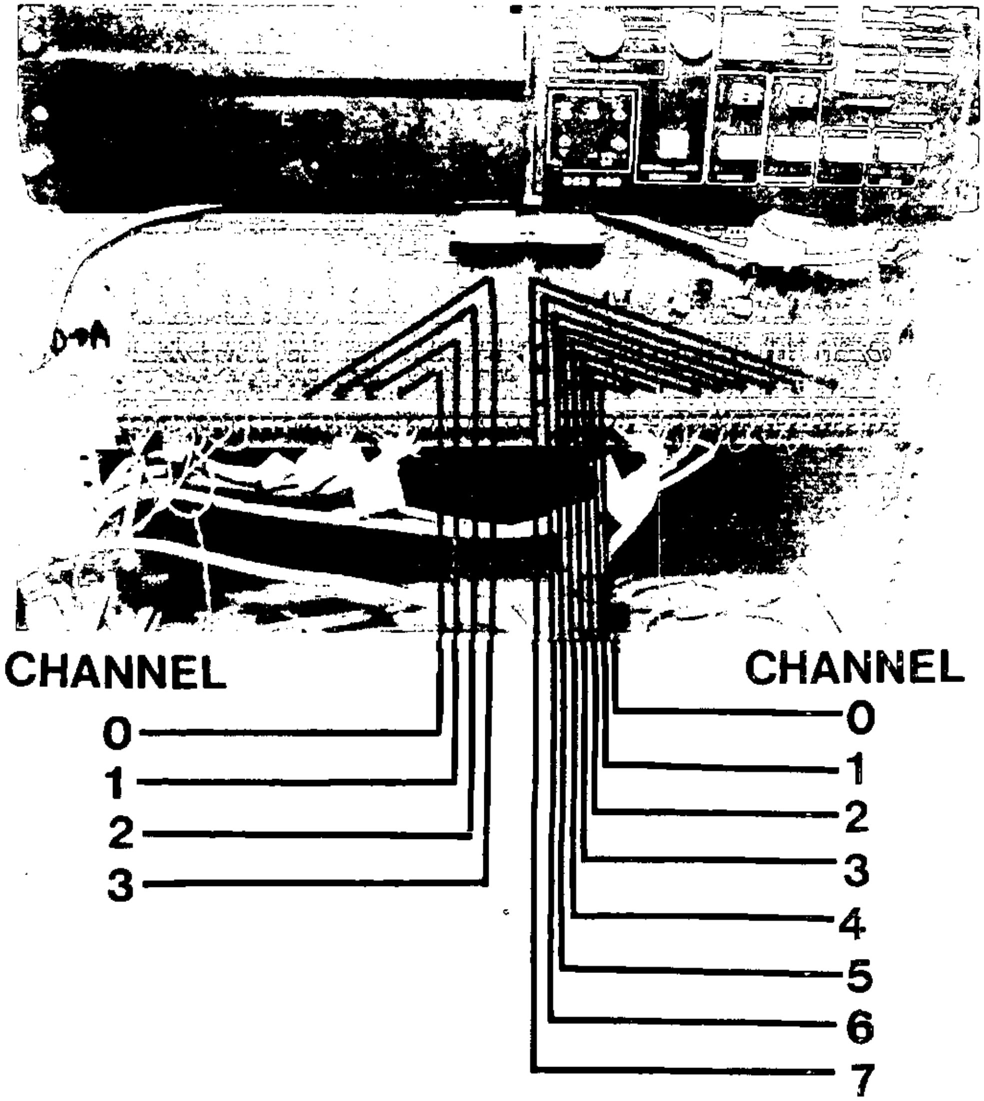


Figure 42. Cahn 1000 Current to Torque Transducer.[165]

through the procedure outlined above. Communication from the LSI-11/23 to the Cahn balance system takes place via a 4-bit binary signal generated in channel 3 of the digital to analog converter. All connections to and from the analog input and output interfaces pass through the DT701 signal conditioning panel. Figure 43 shows the physical layout of the D to A and A to D communications and lists the function each channel is responsible for throughout the laboratory. The 4-bit binary signal from channel 3 of the digital to analog converter is connected to one of 16 demultiplexor/decoder driver on the Cahn balance computer interface control panel shown in Figure 44. The output of the demultiplexor/decoder driver drives 8 dual peripheral drivers which in turn cause magnetic relays to be energized. Although 16 relays could be controlled by this circuit only 8 were needed to control the Cahn balance. The 8 relays utilized were used to control the on-off condition of 6 peripheral devices. The closure of a single relay sets the on-off status of all 6 peripheral functions simultaneously. Table 23 lists the peripheral devices and indicates the significance of its normal or energized state. Table 24 is a logic table revealing the condition of each of the 6 peripheral functions under each of the 9 operational states of the balance. The balance system is placed in a particular state of operation when the equivalent relay number is closed.



<u>Digital to Analog</u>		<u>Analog to Digital</u>	
0	CO Feed	0	Cahn Balance Signal
1	H_2 Feed	1	CO Feed
2	Ar Feed	2	H_2 Feed
3	Cahn Balance Interface/ Control	3	Ar Feed
		4	Thermocouple
		5	Thermocouple
		6	Open
		7	Open

Figure 43 Signal Conditioning Panel

Table 23.

Peripheral Device	Device State
Sorbate Release Solenoid Valve	0 - closed
	1 - open
Rough Down Pump Solenoid Valve	0 - closed
	1 - open
Diffusion Pump Solenoid Actuated Valve	0 - closed
	1 - open
Sample Positioner	0 - raise sample
	1 - lower sample
Programmable Oven	0 - oven off
	1 - start oven program
Heath Kit Autodialer	0 - normal status
	1 - emergency status, send emergency phone call

Table 24. Operational States of the Cahn Balance

Operational State: Relay Number	Peripheral Device State: Sorbate release solenoid valve	Rough Down Pump solenoid valve	Diffusion Pump solenoid valve	Sample Positioner	Programmable Oven	Heath Kit Autodialer
0	0	0	0	0	0	0
1	1	1	0	0	0	0
2	1	1	0	0	1	0
3	0	1	1	0	1	0
4	1	0	1	0	0	0
5	1	0	1	1	0	0
6	0	0	1	0	0	0
7	1	0	0	0	0	0
8	0	0	0	0	0	1

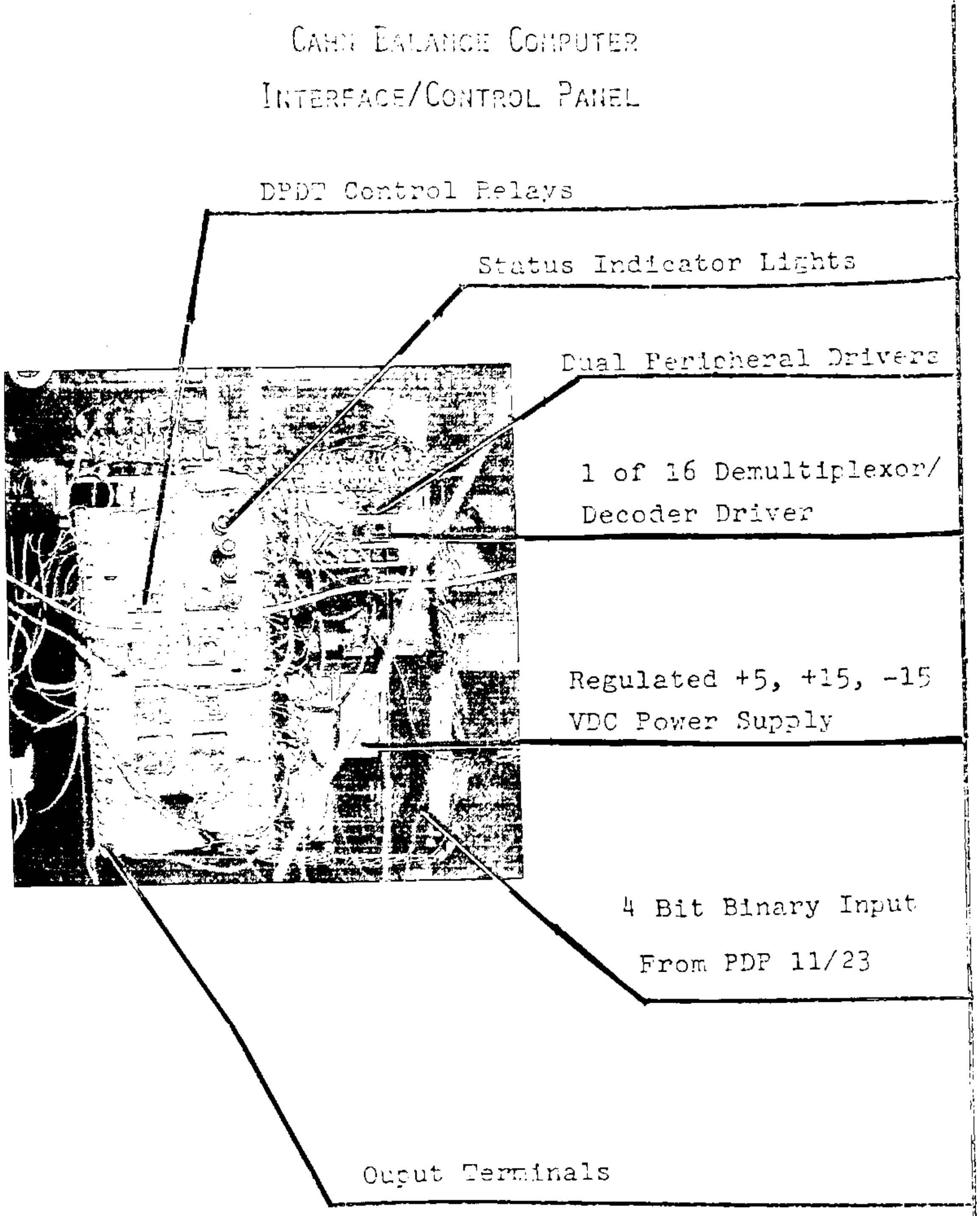
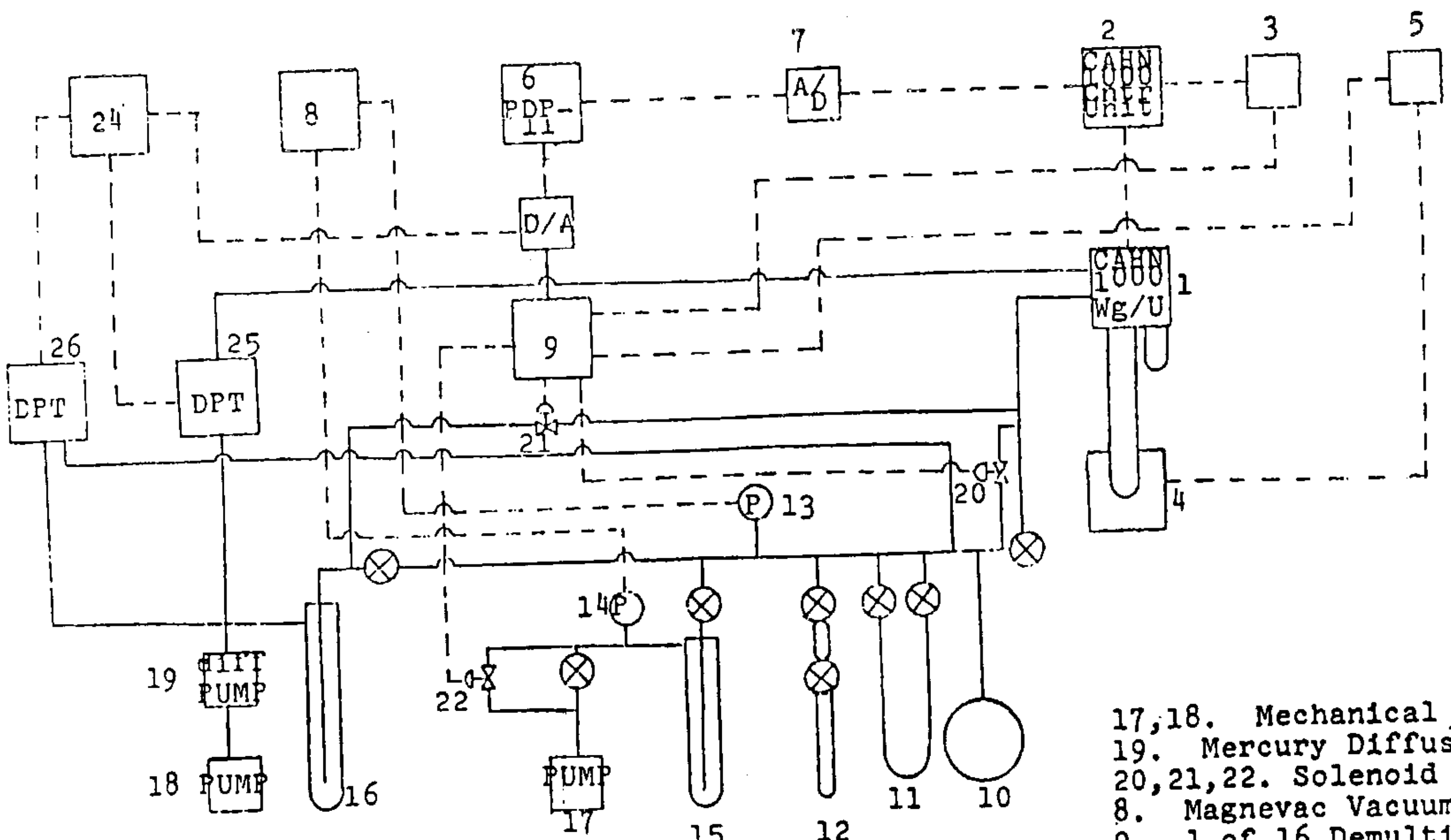


Figure 44. Cahn Balance Computer Interface/Control Panel

The binary number to the demultiplexor/decoder driver is equivalent to the relay number to be energized and to the number of the operational state in which the balance is to be placed. An overall systems schematic of the Cahn balance system is shown in Figure 45 . In this Figure each component of the system is numbered 1 through 26. The dotted lines in the figure correspond to electronic communication pathways between the system components and the solid lines represent the pneumatic connections between the system components. The LSI-11/23 controls all functions involved in the activation of a catalyst sample, measurement of adsorption rates, and graphical output of the sorbtion rate curve with one exception. The sorbate gas must be added to the sorbate storage container to the desired sorbate pressure manually.



1. CAHN 1000 Weighing Unit
2. CAHN 1000 Control Unit
3. Sample Positioner
4. Voltage Programmed Oven
5. Voltage Programmer
6. Microcomputer PDP-11

7. A/D Converter
8. Five-Liter Ball
11. Manometer
12. Sample Tube
13,14. Pressure Transducer
15,16. TRAP

17,18. Mechanical Pump
19. Mercury Diffusion Pump
20,21,22. Solenoid Valve
8. Magnevac Vacuum Gage
9. 1 of 16 Demultiplexer/ Decoder Driver
24. Baratron Differential Pressure Meter
23. Digital to Analog Con.
25. Baratron Diff. Press. transducer
26. Baratron Diff. Press. transducer

Figure 45 Systems Schematic of The Cahn Balance System